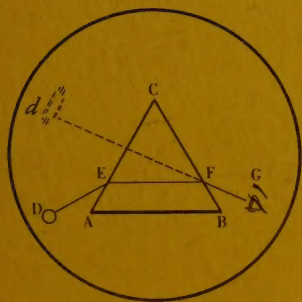


optics and spectroscopy

volume x
number 6
june 1961

OPTICAL SOCIETY OF AMERICA

USSR ACADEMY OF SCIENCES

RUSSIAN EDITORIAL STAFF FOR
OPTIKA I SPEKTROSKOPIYA sponsored by
USSR ACADEMY OF SCIENCES

Editor: S. E. FRISH

Assistant Editor: P. P. FEOFILOV
Corresponding Secretary: L. S. SAZONOV

Associate Editors:

M. M. GUREVICH M. A. EL'IASHEVICH A. A. LEBEDEV V. P. LINNIK
S. L. MANDEL'SHTAM I. V. OBREIMOV V. K. PROKOF'EV
N. N. SOBOLEV A. N. TERENIN A. I. TUDOROVSKII

Translated from *OPTIKA I SPEKTROSKOPIYA* on the initiative of THE OPTICAL SOCIETY OF AMERICA, INC. with a grant-in-aid from THE NATIONAL SCIENCE FOUNDATION. *Optics and Spectroscopy* is a cover-to-cover translation of *Optika i Spektroskopiya* and no attempt is made to edit the material other than to correct obvious misprints. The views are those of the original authors and do not represent the Optical Society of America.

TRANSLATION EDITORIAL STAFF

Scientific Editors

CYRUS FELDMAN, *Oak Ridge National Laboratory*

CARL W. GARLAND, *Massachusetts Institute of Technology*

MATHEW G. GIBBONS, *Oakland, California*

Administrative Editor:

PATRICIA R. WAKELING, *OSA*

Published monthly by the Optical Society of America, Inc. Executive office: 1155 Sixteenth Street, N.W., Washington, D.C. Subscriptions for one year to members of the Society: Associates \$13.00; Regular members and Fellows \$17.00. Subscriptions for non-members of the Society: One year U. S. and Possessions, \$25.00; Foreign \$28.00. Back numbers: \$3.00 per copy. Subscriptions, changes of address and undeliverable copies should be referred to the Executive offices in Washington, D.C. The office of publication is 2500 South State Street, Ann Arbor, Michigan. Second class postage paid at Ann Arbor, Michigan.

TABLES OF ANALYTIC WAVE FUNCTION PARAMETERS OF ATOMS AND IONS

M. G. Veselov, I. M. Antonova, V. F. Brattsev, and I. V. Kirillova (pp. 693-696)

Received 6 July 1960

A variational method was used to calculate the energy and parameters of hydrogenlike analytical functions of the ground state and certain excited states of atoms and ions belonging to isoelectronic sequences having 2, 3, 4 and 5 electrons. The semiempirical formulas suggested in ref. 1 were constructed for these isoelectronic sequences.

1. Hydrogenlike single-electron wave functions of the 1s, 2s, and 2p states were chosen in the form:

$$\left. \begin{aligned} \Psi_{1s} &= \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha r}, \\ \Psi_{2s} &= \sqrt{\frac{3\beta^3}{\pi(\alpha^2 - \alpha\beta + \beta^2)}} \left(1 - \frac{\alpha + \beta}{3} r\right) e^{-\beta r}, \\ \left. \begin{aligned} \Psi_{2p}^{(0)} \\ \Psi_{2p}^{(1)} \\ \Psi_{2p}^{(-1)} \end{aligned} \right\} &= \sqrt{\frac{\gamma^5}{\pi}} r e^{-\gamma r} \begin{cases} \cos \vartheta, \\ \frac{1}{\sqrt{2}} \sin \vartheta e^{i\varphi}, \\ \frac{1}{\sqrt{2}} \sin \vartheta e^{-i\varphi}. \end{cases} \end{aligned} \quad (1)$$

These functions depend on the parameters α , β , and γ , so that the necessary orthogonality and normalization conditions are automatically satisfied. The values of the parameters were found from the conditions for the minimum of the mean value of the energy E .

Only those configurations in which one of the single-electron 2s or 2p states is lacking have been considered in this article. In this case, E will be a function of only two parameters α and β (or α and γ) and can be reduced to the form:

$$E = a^2 T(\mu) - a [ZQ(\mu) - U(\mu)], \quad (2)$$

where Z is the nuclear charge and μ is equal to β/α (or γ/α). Here the first term corresponds to the kinetic energy, the second to the interaction energy with the nucleus, and the third to the energy of interaction of the electrons with each other.

The values of the parameters which yield the minimum (2) will obviously be functions of Z . One may consider the conditions for the minimum, which can conveniently be written in the form²:

$$\left. \begin{aligned} Z &= \frac{2T(\mu)U'(\mu) - T'(\mu)U(\mu)}{2T(\mu)Q'(\mu) - T'(\mu)Q(\mu)}, \\ \alpha &= \frac{ZQ(\mu) - U(\mu)}{2T(\mu)}, \end{aligned} \right\} \quad (3)$$

and the relationship

$$\beta = \alpha\mu \quad (\text{or } \gamma = \alpha\mu)$$

as the parametric definition of these functions. After calculating Z , α , β , (γ) for certain values of μ , we obtain their tabular definitions:

$$\left. \begin{aligned} Z' & \alpha' & \beta' & \text{or} & \gamma', \\ Z'' & \alpha'' & \beta'' & & \gamma'', \\ & \dots & \dots & & \dots \end{aligned} \right\}$$

For integral values of Z , the values of the parameters α and β (or γ) are found by interpolation. The calculations were checked by substituting $\mu = \beta/\alpha$ (or γ/α) into (3). Due to the almost linear dependence of α and

Table 1

	Z	α	β	$-E$	$-E'$	$-E_{\text{exp.}}$	$E' - E_{\text{exp.}}$
1s2s ³ S	2	2.008	0.794	2.172	2.1756	2.1750	-0.0006
	3	3.011	1.222	5.106	5.1104	5.1108	0.0004
	4	4.012	1.733	9.292	9.2974	9.2983	0.0009
	5	5.013	2.339	14.73	14.7367	14.7376	0.0009
	6	6.014	2.742	21.42	21.4287	21.4291	0.0004
	7	7.014	3.245	29.35	29.3745	29.3736	-0.0009
	8	8.014	3.746	38.54	38.5752	38.5722	-0.0030
	9	9.015	4.237	48.91	49.0324	49.0343	0.0019
1s2p ¹ P	2	2.003	0.482	2.122	2.1245	2.1239	-0.0006
	3	3.006	0.970	4.990	4.9930	4.9934	0.0004
	4	4.008	1.465	9.106	9.1108	9.1116	0.0008
	5	5.010	1.963	14.47	14.4796	14.4801	0.0005
	6	6.010	2.461	21.09	21.1003	21.1011	0.0009
	7	7.010	2.960	28.95	28.9740	28.9731	-0.0009
	8	8.010	3.460	38.07	38.1021	38.0990	-0.0031
	9	9.010	3.960	48.43	48.4857	48.4877	0.0020
1s2p ³ P	2	1.991	0.544	2.131	2.1336	2.1330	-0.0006
	3	2.979	1.082	5.023	5.0273	5.0277	0.0004
	4	3.973	1.599	9.170	9.1749	9.1759	0.0010
	5	4.969	2.108	14.567	14.5753	14.5763	0.0010
	6	5.966	2.615	21.22	21.2287	21.2290	0.0003
	7	6.964	3.119	29.11	29.1360	29.1350	-0.0010
	8	7.963	3.622	38.26	38.2982	38.2951	-0.0031
	9	8.962	4.122	48.65	48.7168	48.7189	0.0021
1s2s ² S	3	2.694	0.767	7.414	7.4779	7.4781	0.0002
	4	3.697	1.328	14.26	14.3259	14.3256	-0.0003
	5	4.697	1.858	23.36	23.4285	23.4284	-0.0001
	6	5.698	2.375	34.70	34.7855	34.7857	0.0002
	7	6.698	2.887	48.30	48.3979	48.3983	0.0004
	8	7.698	3.395	64.15	64.2670	64.2667	-0.0003
	9	8.698	3.900	82.25	82.3948	—	—
1s2p ² 2P	3	2.685	0.533	7.351	7.4106	7.4101	-0.0005
	4	3.681	1.063	14.11	14.1799	14.1802	0.0003
	5	4.676	1.591	23.14	23.2072	23.2081	0.0009
	6	5.673	2.110	34.41	34.4911	34.4919	0.0008
	7	6.671	2.623	47.94	48.0317	48.0317	0.0000
	8	7.669	3.133	63.72	63.8308	63.8279	-0.0029
	9	8.667	3.640	81.75	81.8899	81.8915	0.0016
1s2s ² 1S	4	3.708	1.159	14.53	14.6682	14.6682	0.0001
	5	4.713	1.710	24.19	24.3538	24.3529	-0.0009
	6	5.716	2.238	36.36	36.5450	36.5452	0.0002
	7	6.718	2.755	51.03	51.2439	51.2453	0.0013
	8	7.720	3.267	68.20	68.4536	68.4529	-0.0007
	9	8.720	3.776	87.87	88.1772	—	—
1s2p ² 1S	4	3.682	0.815	14.22	14.3343	14.3424	0.0081
	5	4.674	1.346	23.66	23.7692	23.7712	0.0020
	6	5.667	1.869	35.61	35.7188	35.7135	-0.0053
	7	6.662	2.385	50.07	50.1784	50.1729	-0.0055
	8	7.657	2.898	67.03	67.1462	67.1411	-0.0051
	9	8.654	3.407	86.49	86.6217	86.6274	0.0057
1s2p ² 3P	4	3.681	0.875	14.31	14.3969	14.3962	-0.0007
	5	4.672	1.405	23.82	23.9016	23.9023	0.0007
	6	5.665	1.927	35.81	35.9183	35.9192	0.0009
	7	6.660	2.443	50.32	50.4451	50.4458	0.0007
	8	7.655	2.955	67.34	67.4826	67.4795	-0.0031
	9	8.651	3.464	86.85	87.0319	87.0333	0.0014
1s2p ² 1D	4	3.681	0.851	14.27	14.4107	14.4111	0.0004
	5	4.673	1.382	23.75	23.8881	23.8865	-0.0016
	6	5.666	1.904	35.73	35.8798	35.8805	0.0007
	7	6.661	2.420	50.22	50.3833	50.3847	0.0014
	8	7.656	2.931	67.21	67.3986	67.3971	-0.0015
	9	8.653	3.441	86.71	86.9270	86.9274	0.0004
1s2p ² 3S	5	4.673	1.222	24.08	24.2170	—	—
	6	5.663	1.745	36.64	36.7942	36.7941	-0.0001
	7	6.654	2.263	51.96	52.1372	52.1375	0.0003
	8	7.647	2.777	70.05	70.2444	70.2441	-0.0003
	9	8.641	3.287	90.88	91.1163	91.1164	0.0001
1s2p ² 2P	5	4.675	1.183	23.95	24.1839	—	—
	6	5.665	1.706	36.46	36.6723	36.6724	0.0001
	7	6.656	2.225	51.73	51.9395	51.9389	-0.0006
	8	7.649	2.739	69.75	69.9805	69.9812	0.0007
	9	8.643	3.249	90.54	90.7943	90.7940	-0.0003
1s2p ² 2D	5	4.674	1.198	24.00	24.2183	—	—
	6	5.664	1.722	36.53	36.7559	36.7557	-0.0002
	7	6.655	2.240	51.82	52.0626	52.0634	0.0008
	8	7.648	2.754	69.87	70.1362	70.1353	-0.0009
	9	8.642	3.265	90.67	90.9768	90.9771	0.0003

β (or γ) on Z , it turned out to be possible to restrict ourselves to first-order interpolation, for a small table.

The energy was calculated from the formula

$$E = -a^2 T(\mu), \quad (4)$$

which is obtained if one substitutes $ZQ(\mu) - U(\mu)$, taken from (3), into (2).

2. We shall now construct a semiempirical formula for the energy E' as a function of Z .

Let us assume that the dependence of the energy on Z can be represented by the formula

$$E' = -AZ^2 + BZ - \epsilon_0 - \frac{\epsilon_1}{Z} - \rho Z^4. \quad (5)$$

Here the term ρZ^4 acts as a relativistic correction, while the remaining terms are the first terms of the expansion of the energy in powers of Z , on the basis of perturbation theory. For the coefficients A and B , this gives

$$A = T\left(\frac{1}{2}\right),$$

$$B = U\left(\frac{1}{2}\right).$$

The coefficients ϵ_0 , ϵ_1 remained free and were found, along with ρ , by the method of least squares.

3. The results of the calculations are presented in Tables 1 and 2.

The data in the last column of Table 1 show that the experimental values of the energy of atoms and ions agree very well with formula (5). The $1s^2$ term of the $1s^2 2p^2$ configuration, for which the discrepancy between formula (5) and the experimental data exceeds the error*

*This discrepancy can be decreased by taking the superposition of the configurations into account. Refer to ref. 4. of the latter, is an exception.

Table 2

	A	B	ϵ_0	ϵ_1	$\rho \cdot 10^4$
$1s^2 s^3 S$	0.625	0.18793	0.0427	0.0173	0.824
$1s^2 p^1 P$	0.625	0.25987	0.1527	-0.1722	0.743
$1s^2 p^3 P$	0.625	0.22573	0.0663	0.0367	0.801
$1s^2 s^2 s^3 S$	1.125	1.0228	0.3962	0.0727	1.078
$1s^2 p^2 s^3 P$	1.125	1.09353	0.5078	0.1723	1.214
$1s^2 s^2 s^1 S$	1.25	1.57190	0.9475	0.0002	1.809
$1s^2 p^2 s^1 P$	1.25	1.77885	1.2559	0.7689	0.609
$1s^2 p^2 s^1 D$	1.25	1.74721	1.2433	0.4799	1.304
$1s^2 p^2 s^1 S$	1.375	2.52277	2.2417	1.0278	1.377
$1s^2 p^2 s^1 P$	1.375	2.57550	2.2348	2.2013	1.819
$1s^2 p^2 s^1 D$	1.375	2.55441	2.3452	1.3024	1.548

Fairly large systematic deviations also occur in the case of oxygen ions; however, the magnitude of these deviations, on the order of 0.0030, is within the limits of error of the observed ionization potential of the $1s^2$ state of oxygen ions.

We also note that the differences $E' - E_{\text{exp}}$ turn out to be approximately constant in the majority of cases for different values of Z . This implies that the excitation energies and ionization potentials of isoelectronic systems are handled in formulas such as (5) with even greater absolute accuracy than the total energy values.

REFERENCES

1. M. G. Veselov, Zhur. Eksptl. i Teoret. Fiz. **24**, 65 (1953).
2. V. Fok and M. Petrashev, Physik. Z. Sowjetunion **8**, 359 (1935).
3. C. E. Moore, Atomic energy levels as derived from the analysis of optical spectra. U.S. Natl. Bur. Standards Circ. 467, At. Energy Levels **1**, 309 pp. (1949).
4. T. Linderberg and H. Shull, J. Mol. Spectroscopy **5**, 1 (1960).

STUDY OF A DIRECT CURRENT ARC AT INCREASED PRESSURE

A. G. Zhiglinskii, A. N. Zaidel', and E. A. Karklina (pp. 697-701)

Received 20 June 1960

A study has been made of changes in intensity distribution and other properties of a direct current arc excited in a gas at increased pressure. One finds a significant increase in the intensity of spectral lines of a number of elements. This phenomenon is connected, evidently, with a decrease in the diffusion of atoms from the plasma of the arc.

The problem of increasing the sensitivity of spectral analysis amounts to increasing the absolute intensities of spectral lines and the corresponding line-to-background ratios.¹

The intensity of a spectrum excited in an arc is proportional to the concentration of normal atoms in the discharge region and is a function of the arc temperature.² The concentration of normal atoms in the discharge zone is determined by the dynamic equilibrium between the number of atoms entering the discharge and the number of atoms carried away from the discharge zone as a result of diffusion and convection.² The diffusion coefficient is inversely proportional to pressure; consequently, with an increase of pressure the dynamic equilibrium must be shifted in the direction of an increased concentration of

normal atoms in the discharge zone, i.e., the intensity must increase. The role of diffusion will be greatest for light elements, for which the diffusion coefficient is greater. The present experiment therefore used one of the lightest elements—lithium.

The arc was excited in an atmosphere of carbon dioxide whose presence, evidently, has no substantial effect on the intensity of the spectral luminescence or background in the direct current arc.³ An image of the direct current arc, enclosed in a pressure chamber, was projected on the entrance slit (width 25μ) of an ISP-22 spectrograph with the aid of a single condensing lens. At the same time an enlarged image was projected through the opposite window of the chamber onto a screen (this image was used for controlling the distance between

the arc electrodes). The pressure chamber was filled with carbon dioxide gas from a tank containing solid carbon dioxide. A potential of 300 volts dc was applied to the electrodes of the arc.

The pressure chamber arrangement is shown in Fig. 1, which also shows the shape of the carbon electrode. The depth of the crater in the electrode is 4 mm, diameter 3 mm; the outside diameter of the electrode is 5 mm. The necked-in region in the lower part of the electrode has a length of 9 mm and a diameter of 4 mm. The upper conical-tipped electrode (copper) had a diameter of 5 mm at the base. The electrode gap was 1 mm; the discharge current was about 6 amp.

When the pressure in the pressure chamber was increased to 10 atm, there was a significant increase in the intensities of the lithium and copper lines. There was also a decrease in the intensity of the background in the $\lambda \approx 5600$ Å region. A more detailed study of the phenomena in the arc was carried out on Li I 6103 Å. In order to determine the effect of pressure on the intensity of the radiation, the intensity of Li I 6103 Å was studied as a function of time at different pressures (Fig. 2). It is evident from Fig. 2 (curves 2 and 3) that when the pressure of the carbon dioxide was increased to 7 atm, both the intensity and duration of 6103 Å line increased. The experiments were performed with the same amount (0.8 mg) of lithium carbonate. It follows from a comparison of curves 1 and 2 that replacement

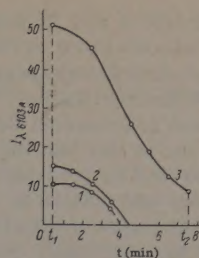


Fig. 2. Lithium burn-out curves. Pressure: curve 1—1 atm air; curve 2—1 atm CO₂; curve 3—7 atm CO₂.

of the air in the pressure chamber by carbon dioxide had little effect on the character of the luminescence of the arc. Hereinafter, all data for 1 atm will refer to an atmosphere of air. The results shown in Fig. 2 were obtained without using any external illumination optics.

The magnitude of the integral $\int_0^{t_0} I dt$, where I is the intensity of the analytical line and t_0 is the burn out time of a weighed sample, is an essential parameter in spectral analysis. The value of this integral (other conditions being equal) determines the absolute sensitivity of spectral analysis.¹ One can determine this value with the aid of the graphs of Fig. 2 from the area bounded by the curves of Fig. 2 and the ordinates passing through points t_1 and t_2 . Calculation showed that the value of the integral for pressures of 4.7 and 10 atm is 4.9 and 10 times as great, respectively, as the value at 1 atm. This situation affected the absolute sensitivity of lithium detection in the following way: the photographic density of Li I 6103 Å produced by a 30 mg sample at 1 atm was the same as that produced by a 2-3 mg sample at 7 atm of carbon dioxide.

In order to determine the effect of pressure on line to background ratios, a study was made of the time variation of the intensity of Li 6103 Å and the adjacent background I_B at different pressures p . The value of the ratio I_L/I_B (see the table) was calculated. It is clear from the table that as the pressure in the chamber increased not only did Li I 6103 Å increase in intensity, but the background intensity decreased as well.* As a result, the

*In an investigation of the intensity increase with increased pressure of lines of various other elements a substantial intensity decrease of the background was not observed.

time-averaged value of I_L/I_B increased by almost an order of magnitude (see the last line of the table) when the pressure was raised to 7 atm (for this experiment the entrance slit was illuminated without a condenser). With regard to the relative sensitivity of detecting lithium in sodium, for example, it turned out that the line/back-

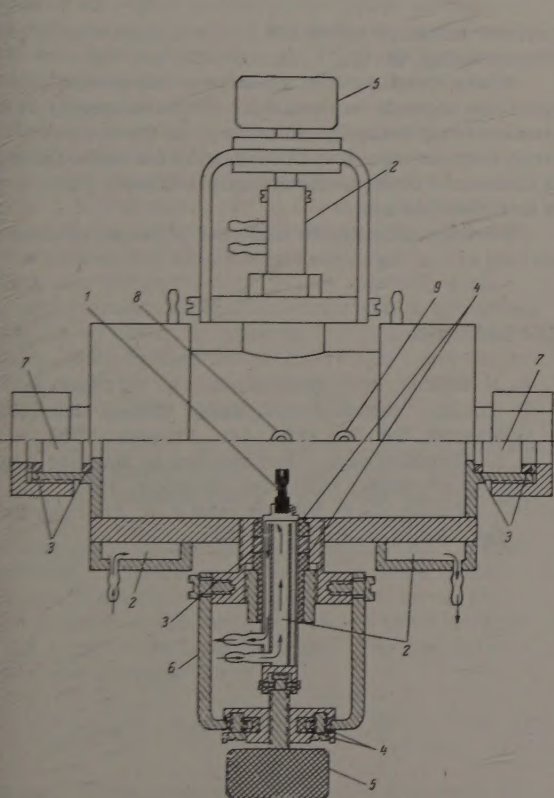


Fig. 1. Construction of the pressure chamber. 1—arc electrodes; 2—water-cooling system; 3—rubber seals; 4—insulating hard rubber washer; 5—handle for adjusting the electrodes; 6—fastening bracket; 7—window; 8—connection for gas supply; 9—spring safety valve.

t (min)	p = 1 atm			p = 4 atm			p = 7 atm		
	I_L	I_B	I_L/I_B	I_L	I_B	I_L/I_B	I_L	I_B	I_L/I_B
1	64	84	0.72	108	21	5.2	212	29	7.3
2	52	71	0.72	139	27	5.2	281	29	9.7
3	49	46	1.05	110	14	7.8	213	27	7.9
4	24	29	0.82	113	16	8.1	188	26	7.2
5				96	10	9.5	161	13	12.4
6				45	6	7.5	172	18	9.5
7				70	9	7.8	152	18	8.5
8							122	10	12.2
—	—	—	~0.8*	—	—	~7*	—	—	~9*

*Average value for all exposure times.

ground ratio for Li I 6103 A at 0.3% lithium concentration and 1 atm pressure was the same as for a 0.001% lithium concentration and a carbon dioxide pressure of 7 atm.

In order to study the distribution of intensity in the arc, an image of it was projected on the entrance slit of the spectrograph in such a way that the axis of the discharge was either parallel or perpendicular to it. In the second case, the image was rotated by means of two mirrors. In both cases the image of the electrodes was disposed approximately symmetrically relative to the spectrograph slit. The slit-width was 0.06 mm; the exposure in the first case was 7 sec and in the second 0.01 sec. The exposure was kept short in the second case so that the discharge would not change its position relative to the electrodes during the exposure. In the first case it was not necessary to satisfy this condition, since the intensity distribution along the axis of the discharge evidently changed little with time.

Certain of the relations obtained are given in Fig. 3. In this figure, distances along the photographic plate are plotted as abscissae. It is evident from Fig. 3a that with respect to Li I 6103 A radiation, there is a contraction of the discharge perpendicular to its axis. Examination of a number of curves like those shown in Fig. 3a indicated that their half-widths for 1, 7, and 10 atm were approximately in the ratio 6:3:2. At the same time, observation of the image with the slit parallel to the axis of the discharge (Fig. 3b) indicated that the intensity of the arc increased with increasing pressure.

Parallel with the study of intensity change and contraction of the discharge, the variation of temperature in the arc was studied by Ornstein's method using Cu 5105 and 5153 A.

It was found that when the pressure increased to 7 atm, the temperature of the arc (approximately 6000°K) increased by about 700°. Such an increase could not produce the observed change in intensity by changing the population of the lithium energy levels. This makes it reasonable to suggest that the increase in intensity with increasing pressure may be due chiefly to an increase in the concentration of normal atoms in the discharge. A decrease of the diffusion coefficient with increased pressure in the pressure chamber is the probable cause of this. The lower sample consumption at higher pressures can be attributed to the increase in boiling point under these conditions.

The effect of pressure on the arc spectra of other elements was also investigated. An increase in the intensity of the spectrum was also detected for Na, Al, Cu, Zn, Fe, Sb, and N at higher pressures. At the present

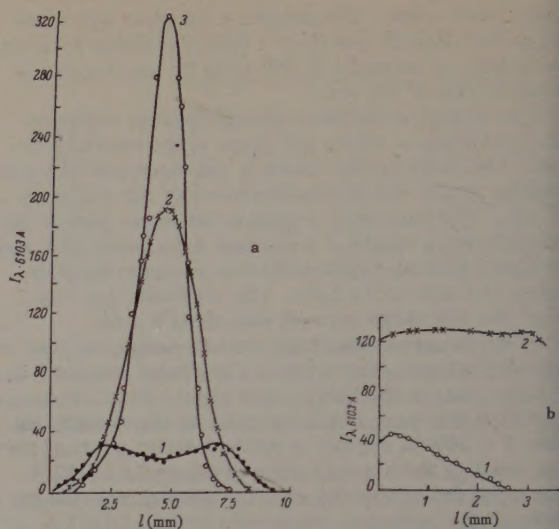


Fig. 3. Intensity distribution in a direct current arc with increasing pressure. a—axis of the discharge perpendicular to the spectrograph slit; b—axis of the discharge parallel to the spectrograph slit. Pressure (in atm): curve 1—1; curve 2—7, curve 3—10.

time the indicated effect has not been observed in certain elements (Mg, Si, Cu, V, Mn, Cd, Sr, and Pb).

It was found that the increase in the intensity of the spectrum depends on the nature of the sample in which the element being investigated occurs. In the spectrum of a given element, the intensity increase for different lines is different. Pressure broadening evidently plays a role in this phenomenon.

We are continuing to study the behavior of the direct current arc at high pressures.

REFERENCES

1. A. N. Zaidel', N. I. Kaliteevskii, L. V. Lipis, and M. P. Chaika, "Spectral Analysis of Atomic Materials." Gosudarst. Izd. Fiz.-Mat. Lit., Moscow, 1960.
2. S. L. Mandel'shtam, "Introduction to Spectral Analysis." Gosudarst. Tekh. Izd., Moscow, 1946.
3. B. L. Vallee, C. B. Reimer, and J. R. Loofbourow, J. Opt. Soc. Am. 40, 751 (1950).

ON THE APPLICABILITY OF THE ZERO-TH APPROXIMATION OF THE GENERALIZED VALENCE-OPTICAL SCHEME

L. M. Sverdlov (pp. 702-706)

Received 23 June 1960

To clarify the applicability of the zeroth approximation of the generalized valence-optical scheme, in which it is assumed that the direction of the dipole moment of the bond does not coincide with the direction of the bond itself, the calculation of the electro-optical parameters of the methyl halides (CH_3Cl , CD_3Cl , CH_3Br , CD_3Br , CH_3I , CD_3I) is carried out. It is shown that in this approximation fundamental difficulties of the theory are not completely removed. Therefore, for the calculation of the intensities of infrared spectra and of the electro-optical parameters of polyatomic molecules one can use only the first approximation of the generalized valence-optical scheme. As an example, a calculation of the electro-optical parameters of sulfur dioxide is carried out in the first approximation of the generalized valence-optical scheme. The numerical values obtained coincide with the results of the calculation in the first approximation of the valence-optical scheme.

1. In ref. 1 we formulated in zeroth and first approximations the generalized valence-optical scheme in which it was assumed that the direction of the dipole moment of the bond does not coincide with the direction of the bond itself. In view of the fact that in the first approximation of the generalized valence-optical scheme the formulas for $\partial P / \partial Q_e$ have a very complex form, the question arises about the possibility of limiting oneself to the zeroth approximation of the generalized valence-optical scheme for calculations of intensities of infrared spectra. In ref. 1 it was shown that in the case of triatomic molecules one can limit oneself to the zeroth approximation of the generalized scheme.

It is of interest to examine in this approximation the complex molecules in which deformation vibrations of various forms occur, in order to clarify the internal consistency of the results obtained. We will carry out a calculation of the electro-optical parameters of the methyl halides CX_3Z ($\text{X} = \text{H}, \text{D}$; $\text{Z} = \text{Cl}, \text{Br}, \text{I}$).

2. From symmetry considerations it follows that the component of the dipole moment of the $\text{C}-\text{X}^{(n)}$ bond, perpendicular to the plane in which are located the $\text{C}-\text{Z}$ and $\text{C}-\text{X}^{(n)}$ bonds, is equal to zero and, accordingly, the dipole moment of the $\text{C}-\text{X}^{(n)}$ bond lies in the $\text{ZCX}^{(n)}$ plane. From analogous considerations the components of the dipole moment of the $\text{C}-\text{Z}$ bond are equal to zero, i.e., the dipole moment of this bond is directed along the line joining the nuclei of the C and Z atoms. The general dipole moment of the molecule is

$$P = \mu_{||}^{\text{CZ}} - 3\cos\theta \cdot \mu_{||}^{\text{CX}} + 3\sin\theta \cdot \mu_{\perp}^{\text{CX}}. \quad (1)$$

Here $\mu_{||}^{\text{CX}}$ is the component of the dipole moment of the $\text{C}-\text{X}$ bond, directed along the $\text{C}-\text{X}$ bond, $\mu_{\perp}^{\text{CX}}$ is the component of the dipole moment of this bond perpendicular to the bond and lying in the $\text{ZCX}^{(n)}$ plane.

Applying formulas (12)-(15) of ref. 1, we obtain the derivatives of the dipole moment with respect to the normal coordinates in the first approximation of the generalized valence-optical scheme.

$$\begin{aligned} \frac{\partial P_{\xi}}{\partial Q_i^{A_1}} = & \left\{ \left[\frac{\partial \mu_{\text{CZ}}}{\partial q_0} - 3\cos\theta \left(\frac{\partial \mu_{||}^{(1)}}{\partial q_0} - \tan\theta \frac{\partial \mu_{\perp}^{(1)}}{\partial q_0} \right) - 3\sin\theta \left(\mu_{||}^{(1)} + \cot\theta \cdot \mu_{\perp}^{(1)} \right) \frac{\partial \varphi_1}{\partial q_0} \right] C_{oi}^{A_1} \right. \\ & + \left[-\sqrt{3} \cos\theta \left(\left(\frac{\partial \mu_{||}^{(1)}}{\partial q_1} - \tan\theta \frac{\partial \mu_{\perp}^{(1)}}{\partial q_1} \right) + 2 \left(\frac{\partial \mu_{||}^{(2)}}{\partial q_1} - \tan\theta \frac{\partial \mu_{\perp}^{(2)}}{\partial q_1} \right) \right) \right. \\ & + \left. \left. \sqrt{3} \frac{\partial \mu_{\text{CZ}}}{\partial q_1} - \sqrt{3} \sin\theta \left(\mu_{||}^{(1)} + \cot\theta \cdot \mu_{\perp}^{(1)} \right) \left(\frac{\partial \varphi_1}{\partial q_1} + 2 \frac{\partial \varphi_2}{\partial q_1} \right) \right] C_{oi}^{A_1} \right. \\ & + \left[-\sqrt{3} \sin\theta \left(\frac{\mu_{||}^{(1)}}{r_{\text{CX}}} + \cot\theta \cdot \frac{\mu_{\perp}^{(1)}}{r_{\text{CX}}} \right) - \sqrt{3} \cos\theta \left(\left(\frac{\partial \mu_{||}^{(1)}}{\partial \varphi_1} - \tan\theta \frac{\partial \mu_{\perp}^{(1)}}{\partial \varphi_1} \right) \right. \right. \\ & + \left. \left. 2 \left(\frac{\partial \mu_{||}^{(2)}}{\partial \varphi_1} - \tan\theta \frac{\partial \mu_{\perp}^{(2)}}{\partial \varphi_1} \right) \right) + \sqrt{3} \frac{\partial \mu_{\text{CZ}}}{\partial \varphi_1} \right] E_i^{A_1} \Big\}; \quad (2) \end{aligned}$$

$$\frac{\partial P_{\xi}}{\partial Q_i^{A_1}} = \frac{\partial P_{\eta}}{\partial Q_i^{A_1}} = 0 \quad (l = 1, 2, 3).$$

$$\begin{aligned} \frac{\partial P_{\eta}}{\partial Q_i^{E_{II}}} = & \left\{ \left[\sqrt{\frac{3}{2}} \sin\theta \left(\left(\frac{\partial \mu_{||}^{(1)}}{\partial q_1} + \cot\theta \cdot \frac{\partial \mu_{\perp}^{(1)}}{\partial q_1} \right) - \left(\frac{\partial \mu_{||}^{(2)}}{\partial q_1} + \cot\theta \frac{\partial \mu_{\perp}^{(2)}}{\partial q_1} \right) \right) \right. \right. \\ & - \left. \left. \sqrt{\frac{3}{2}} \cos\theta \left(\mu_{||}^{(1)} - \tan\theta \cdot \mu_{\perp}^{(1)} \right) \left(\frac{\partial \varphi_1}{\partial q_1} - \frac{\partial \varphi_2}{\partial q_1} \right) \right] C_{oi}^{E_{II}} \right. \\ & + \left[-\sqrt{\frac{3}{2}} \cos\theta \left(\frac{\mu_{||}^{(1)}}{r_{\text{CX}}} - \tan\theta \cdot \frac{\mu_{\perp}^{(1)}}{r_{\text{CX}}} \right) \right. \\ & + \left. \sqrt{\frac{3}{2}} \sin\theta \left(\frac{1}{r_{\text{CX}}} \left(\frac{\partial \mu_{||}^{(1)}}{\partial \varphi_1} + \cot\theta \frac{\partial \mu_{\perp}^{(1)}}{\partial \varphi_1} \right) \right. \right. \\ & - \left. \left. \frac{1}{r_{\text{CX}}} \left(\frac{\partial \mu_{||}^{(2)}}{\partial \varphi_1} + \cot\theta \frac{\partial \mu_{\perp}^{(2)}}{\partial \varphi_1} \right) \right) \right] E_i^{E_{II}} \\ & + \left[-\sqrt{\frac{3}{2}} \sin\theta \left(\frac{\mu_{||}^{(1)}}{r_{\text{CX}}} + \cot\theta \frac{\mu_{\perp}^{(1)}}{r_{\text{CX}}} \right) \right] F_i^{E_{II}} + \left[\frac{\mu_{\text{CZ}}}{r_{\text{CX}}} \right] G_i^{E_{II}} \Big\}; \quad (3) \end{aligned}$$

$$\frac{\partial P_{\xi}}{\partial Q_i^{E_{II}}} = \frac{\partial P_{\zeta}}{\partial Q_i^{E_{II}}} = 0 \quad (l = 4, 5, 6).$$

If we equate to zero the quantities characterizing the perpendicular components of the dipole moments of the bonds ($\mu_{\perp}$, $\partial\mu_{\perp}/\partial q_0$, $\partial\mu_{\perp}^{(1)}/\partial q_1$, $\partial\mu_{\perp}^{(2)}/\partial q_1$, $\partial\mu_{\perp}/\partial\varphi$) in formulas (2) and (3), we obtain the formulas for $\partial P/\partial Q_1$ in the first approximation of the valence-optical scheme (refer to formulas (10a) and (10b) of ref. 2).

If we equate to zero the quantities characterizing the interaction between different elements of the molecule ($\partial\mu^{(1)}/\partial q_1$, $\partial\mu/\partial\varphi$, $\partial\varphi/\partial q_1$) in formulas (2) and (3), we obtain an expression for $\partial P/\partial Q_1$ in the zeroth approximation of the generalized valence-optical scheme.

For the calculation of the electro-optical parameters in the zeroth approximation of the generalized valence-optical scheme we used values of the coefficients L_{kl} and L_{kl}^{-1} and numerical values of the derivatives of the dipole moments with respect to the symmetry coordinates of type A_1 : $\partial P/\partial q^{A_1}$, $\partial P/\partial\varphi^{A_1}$, $\partial P/\partial q_0^{A_1}$, derived in ref. 2. The derivatives of the dipole moment with respect to the symmetry coordinates of type E: $\partial P/\partial\varphi^E$, $\partial P/\partial\varphi^E$, $\partial P/\partial\psi^E$ were calculated anew on the basis of the experimental values of $\partial P/\partial Q_1$ of the CH_3Z and CD_3Z molecules, according to the scheme detailed in ref. 2. For the combination of signs of $\partial P/\partial Q_1$ which we chose in ref. 2 ($+\partial P/\partial Q_1^{A_1}$, $-\partial P/\partial Q_1^{A_1}$, $-\partial P/\partial Q_1^{A_1}$, $+\partial P/\partial Q_1^{A_1}$, $-\partial P/\partial Q_1^E$, $+\partial P/\partial Q_1^E$), we obtain the following results:

CH_3Cl AND CD_3Cl MOLECULES

Symmetry type A_1 :

$$\frac{\partial\mu_{C-Cl}}{\partial q_0} = -2.2443 \frac{D}{\text{\AA}}. \quad (4)$$

Symmetry type A_1 and E:

$$\frac{\partial\mu_{||}^{CH}}{\partial r_1} = 0.1486 \frac{D}{\text{\AA}}; \quad \frac{\partial\mu_{\perp}^{CH}}{\partial q_1} = 0.3576 \frac{D}{\text{\AA}}; \quad (5)$$

$$\mu_{||}^{CH} = -0.184 D; \quad \mu_{\perp}^{CH} = 0.0547 D. \quad (6)$$

Symmetry type E:

$$\left. \begin{aligned} \mu_{||}^{CH} &= -0.4841 D; \quad \mu_{\perp}^{CH} = -0.0391 D; \\ \mu_{C-Cl} &= 1.5489 D. \end{aligned} \right\} \quad (7)$$

CH_3Br AND CD_3Br MOLECULES

Symmetry type A_1 :

$$\frac{\partial\mu_{C-Br}}{\partial q_0} = -1.501 \frac{D}{\text{\AA}}. \quad (8)$$

Symmetry type A_1 and E:

$$\frac{\partial\mu_{||}^{CH}}{\partial q_1} = 0.083 \frac{D}{\text{\AA}}; \quad \frac{\partial\mu_{\perp}^{CH}}{\partial q_1} = 0.3259 \frac{D}{\text{\AA}}; \quad (9)$$

$$\mu_{||}^{CH} = -0.2678 D; \quad \mu_{\perp}^{CH} = 0.004 D. \quad (10)$$

Symmetry type E:

$$\mu_{||}^{CH} = -0.4829 D; \quad \mu_{\perp}^{CH} = -0.0621 D; \quad \mu_{C-Br} = 1.5528 D. \quad (11)$$

CH_3I AND CD_3I MOLECULES

Symmetry type A_1 :

$$\frac{\partial\mu_{C-I}}{\partial q_0} = -0.6408 \frac{D}{\text{\AA}}. \quad (12)$$

Symmetry type A_1 and E:

$$\frac{\partial\mu_{||}^{CH}}{\partial q_1} = +0.0548 \frac{D}{\text{\AA}}; \quad \frac{\partial\mu_{\perp}^{CH}}{\partial q_1} = 0.2363 \frac{D}{\text{\AA}}; \quad (13)$$

$$\mu_{||}^{CH} = -0.3718 D; \quad \mu_{\perp}^{CH} = 0.016 D. \quad (14)$$

Symmetry type E:

$$\mu_{||}^{CH} = -0.475 D; \quad \mu_{\perp}^{CH} = -0.0149 D; \quad \mu_{C-I} = 1.2541 D. \quad (15)$$

3. The calculations carried out for the methyl halides (i.e., molecules in which the deformation vibrations belong in several symmetry types) show that even in the zeroth approximation of the generalized valence-optical scheme a fundamental difficulty of the theory is not removed. Indeed, for one and the same combination

$$\left(\frac{\mu_{||}^{CH}}{r_{CH}} + \cot\theta \cdot \frac{\mu_{\perp}^{CH}}{r_{CH}} \right)$$

we have obtained different numerical values from the intensities of vibrations of types A_1 and E. If still another combination of the parameters $\mu_{||}$ and $\mu_{\perp}$ is used, and specifically

$$\left(\frac{\mu_{||}^{CH}}{r_{CH}} - \tan\theta \cdot \frac{\mu_{\perp}^{CH}}{r_{CH}} \right),$$

then for the components of the dipole moment $\mu_{||}^{CH}$ and $\mu_{\perp}^{CH}$ we obtain different values for the vibrations of different symmetry types [refer to (6) and (7), (10) and (14) and (15)]. At the same time for the derivatives of the dipole moment with respect to changes of the bond length, the difficulty indicated vanishes (as also in the case of the SO_2 molecule, ref. 1). However, it must be noted that the derivative of the dipole moment component perpendicular to the bond with respect to the bond length $\partial\mu_{\perp}^{CH}/\partial q_1$ for all of the methyl halides is larger than the derivative of the dipole moment component parallel to the bond with respect to the bond length $\partial\mu_{||}^{CH}/\partial q_1$.

Thus, taking account of the results obtained for the methyl halides, we arrive at the important conclusion that for the calculation of the intensities of infrared spectra and of the electro-optical parameters of polyatomic molecules the inclusion of all interactions is obligatory, i.e., it is necessary to use the first approximation of the generalized valence-optical scheme in which the dependence of the components of the dipole moment of a specific bond on the changes of the values of the angles and on the changes of the lengths of other bonds must be taken into account.

4. We will examine how the results obtained in the first approximation of the generalized valence-optical scheme will differ from the results of the first approximation of the valence-optical scheme.

First, the expressions for the electro-optical parameters become more complex: the combinations will include not only the initial terms $\mu_{||}^{(0)}$, $\partial\mu_{||}^{(0)}/\partial q_1$, $\partial\mu_{||}^{(0)}/\partial\varphi$, but also additional terms characterizing the perpendicular components of the dipole moment $\mu_{\perp}^{(0)}$, $\partial\mu_{\perp}^{(0)}/\partial q_1$, $\partial\mu_{\perp}^{(0)}/\partial\varphi$.

Secondly, in the first approximation of the generalized valence-optical scheme one can, as a rule, only define combinations of the electro-optical parameters: in particular, combinations of the components of the dipole moment $\mu_{||}$ and $\mu_{\perp}$ and not the components themselves.

For example, for the triatomic molecule sulfur

vide we obtain the following combinations of the electro-optical parameters in the approximation indicated*

for their calculation we used formulas (25) and (26) of [1] and the results of the solution of the mechanical problem from ref. 3.

$$\begin{aligned}
 & [\mu_{||}^{SO} + \tan \theta \cdot \mu_{\perp}^{SO}] = 1.5872 D; \\
 & \left[\frac{\mu_{||}^{SO}}{r_{SO}} + \tan \theta \cdot \frac{\mu_{\perp}^{SO}}{r_{SO}} \right] = 1.1084 \frac{D}{\text{\AA}}; \\
 & \left\{ \left(\frac{\partial \mu_{||}^{(1)}}{\partial \varphi_1} + \frac{\partial \mu_{||}^{(2)}}{\partial \varphi_1} \right) + \tan \theta \cdot \left(\frac{\partial \mu_{\perp}^{(1)}}{\partial \varphi_1} + \frac{\partial \mu_{\perp}^{(2)}}{\partial \varphi_1} \right) + \frac{1}{\cos^2 \theta} \mu_{\perp}^{(2)} \right\} \frac{1}{2r_{SO}} = -0.8336 \frac{D}{\text{\AA}}; \\
 & \left\{ \left[\frac{\partial \mu_{||}^{(1)}}{\partial q_1} + \mu_{||} \left(\cot 2\theta \cdot \frac{\partial \varphi_1}{\partial q_1} - \operatorname{cosec} 2\theta \cdot \frac{\partial \varphi_2}{\partial q_1} \right) + a \left(\frac{\partial \mu_{||}^{(1)}}{\partial \varphi_1} - \frac{\partial \mu_{||}^{(2)}}{\partial \varphi_1} \right) \frac{1}{2r_{SO}} \right] + \left[\left(-\cot 2\theta \cdot \frac{\partial \mu_{\perp}^{(1)}}{\partial q_1} + \operatorname{cosec} 2\theta \cdot \frac{\partial \mu_{\perp}^{(2)}}{\partial q_1} \right) + \mu_{\perp} \frac{\partial \varphi_1}{\partial q_1} - a \cot \theta \cdot \left(\frac{\partial \mu_{\perp}^{(1)}}{\partial \varphi_1} - \frac{\partial \mu_{\perp}^{(2)}}{\partial \varphi_1} \right) \frac{1}{2r_{SO}} \right] \right\} = -5.2706 \frac{D}{\text{\AA}}; \\
 & \left\{ \left[\frac{\partial \mu_{||}^{(2)}}{\partial q_1} + \mu_{||} \left(-\operatorname{cosec} 2\theta \cdot \frac{\partial \varphi_1}{\partial q_1} + \cot 2\theta \cdot \frac{\partial \varphi_2}{\partial q_1} \right) - a \left(\frac{\partial \mu_{||}^{(1)}}{\partial \varphi_1} - \frac{\partial \mu_{||}^{(2)}}{\partial \varphi_1} \right) \frac{1}{2r_{SO}} \right] + \left[\operatorname{cosec} 2\theta \cdot \frac{\partial \mu_{\perp}^{(1)}}{\partial q_1} - \cot 2\theta \cdot \frac{\partial \mu_{\perp}^{(2)}}{\partial q_1} + \mu_{\perp} \frac{\partial \varphi_2}{\partial q_1} + a \cdot \cot \theta \cdot \left(\frac{\partial \mu_{\perp}^{(1)}}{\partial \varphi_1} - \frac{\partial \mu_{\perp}^{(2)}}{\partial \varphi_1} \right) \frac{1}{2r_{SO}} \right] \right\} = 0.1565 \frac{D}{\text{\AA}}.
 \end{aligned} \tag{16}$$

Comparing these values with the results obtained in the first approximation of the valence-optical scheme (refer to Table 7 of ref. 3) we see that the numerical values of the combinations have not changed. However, in each formula there have appeared new terms connected with the perpendicular components of the bond dipole moment. Therefore, in carrying out calculations of the intensities of infrared spectra of polyatomic molecules one can limit oneself to the first approximation of the valence-optical scheme (not forgetting the omitted terms characterizing the perpendicular components of the dipole moments). In that case, if one makes a comparison of the numerical values of the electro-optical parameters determined from the intensities of infrared spectra with the values obtained with the assistance of quantum-mechanical calculations, then it is necessary to take account of all of the terms connected with both the parallel and the perpendicular components of the dipole moments.

REFERENCES

1. L. M. Sverdlov, Opt. i Spekt. 10, 152 (1961), Optics and Spectroscopy 10, 76 (1961).
2. L. M. Sverdlov, Opt. i Spekt. 6, 729 (1959), Optics and Spectroscopy 6, 477 (1959).
3. L. M. Sverdlov, Opt. i Spekt. 7, 152 (1959), Optics and Spectroscopy 7, 97 (1959).

VIBRATIONAL SPECTRUM AND FORCE FIELD OF THE TRIMETHYLCHLOROSILANE MOLECULE

I. F. Kovalev (pp. 707-712)

Received 9 July 1960

Potential energy constants are calculated. Frequencies and forms of the vibrational spectrum are computed. An interpretation of the fundamental frequencies is carried out.

INTRODUCTION

In connection with the widespread application of silico-organic compounds, a knowledge of their physico-chemical properties is needed, particularly of their vibrational spectra and the force distribution within the molecules. It is appropriate to perform, as a first stage, a detailed study of the simplest representatives—for example, the methylhalosilanes. We have investigated a homologous series of methylchlorosilanes.

Certain isolated questions have previously been solved for these compounds. Thus, Kriegsmann,¹ basing his work on the results of an approximate evaluation of the forces which indicate the stiffness of the individual bonds and angles, draws certain conclusions on the character of the bonds in various silicon compounds, and on the strengthening or weakening of the bonds through the influence of adjacent substituents. Shimizu and Murata,^{2,3*}

*References to the works of other authors in this field are given in refs. 1-3.

assuming a Urey-Bradley potential function, have carried out a calculation of the vibrational spectra of $(\text{CH}_3)_n\text{SiCl}_{4-n}$ ($n = 1-3$).

At the present time, new experimental data on the spectra of the methylchlorosilanes have appeared. In particular, Ignat'eva, Bazhulin, and Baeva⁴ have measured the intensities of the infrared bands and have discovered regularities in their changes as chlorine atoms accumulate on the silicon.

Accordingly, it is desirable to carry out a more detailed theoretical investigation of the compounds cited.

In the present work, the results of a calculation of the frequencies, the forms of the normal vibrations, and the constants of the force-field are examined for the trimethylchlorosilane molecule.* A calculation of the in-

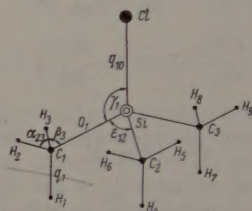
*The results of the study of CH_3SiCl_3 and $(\text{CH}_3)_2\text{SiCl}_2$ were reported at the XIII Conference on Spectroscopy in Leningrad.

tensities will be the next stage of the work

CALCULATION OF THE FREQUENCIES, FORMS OF THE NORMAL VIBRATIONS, AND FORCE COEFFICIENTS

In solving the problem, we made use of the experimental data on the infrared and Raman spectra published in refs. 5 and 6 and of the information obtained during the calculation of the methylsilanes.⁷ The procedure of Vol'kenshtein, El'yashevich, and Stepanov⁸ and of Mayants⁹ was followed.

The model of the $(\text{CH}_3)_3\text{SiCl}$ molecule (see figure) belongs to the symmetry point group C_{3v} . Accordingly, the following internal coordinates were chosen: Q_i ($i = 1-3$) — $\Delta(\text{Si}-\text{C})$, q_i ($i = 1-9$) — $\Delta(\text{C}-\text{H})$, q_{10} — $\Delta(\text{Si}-\text{Cl})$, α_{ij} ($i, j = 1-9$; $i \neq j$) — $\Delta(\text{HCH})$, β_i ($i = 1-9$) — $\Delta(\text{HCSi})$, ϵ_{ij} ($i, j = 1-3$; $i \neq j$) — $\Delta(\text{CSiC})$, γ_i ($i = 1-3$) — $\Delta(\text{CSiCl})$.



Equilibrium configuration of the trimethylchlorosilane molecule.

The following were taken as geometrical parameters: $r(\text{Si}-\text{C}) = 1.89$, $r(\text{Si}-\text{Cl}) = 2.09$, $r(\text{C}-\text{H}) = 1.093$ Å, tetrahedral angles. The complete field of description of the vibrations for $(\text{CH}_3)_3\text{SiCl}$ breaks down into irreducible representations according to the rule:

$$\Gamma = 8A_1 + 4A_2 + 12E,$$

the vibrations of type A_2 being forbidden. There were additional relations among the changes in the angles:

$$\left. \begin{aligned} \epsilon_{12} + \epsilon_{23} + \epsilon_{13} + \gamma_1 + \gamma_2 + \gamma_3 &= 0, \\ \alpha_{12} + \alpha_{23} + \alpha_{13} + \beta_1 + \beta_2 + \beta_3 &= 0, \\ \alpha_{45} + \alpha_{56} + \alpha_{46} + \beta_4 + \beta_5 + \beta_6 &= 0, \\ \alpha_{78} + \alpha_{89} + \alpha_{79} + \beta_7 + \beta_8 + \beta_9 &= 0. \end{aligned} \right\}$$

The secular equations (8th order for type A_1 , 3rd for type A_2 , and 11th for type E),* which were obtained after

*Two torsional vibrations of the CH_3 groups were not considered.

taking account of the symmetry properties and the conditions (2), were solved by Mayants's iteration method.^{9*}

*The author thanks A. M. Bogomolov for a partial solution of the equations with the help of the "Ural" electronic computer.

The results are recorded in Tables 1-3.

The force coefficients have been calculated by the variation method, CH_3SiCl_3 , $(\text{CH}_3)_2\text{SiCl}_2$, and $(\text{CH}_3)_4\text{Si}^{10}$ being considered at the same time. For trimethylchlorosilane, only 3 coefficients were actually unknown: $k_\gamma(\text{ClSiC})$, $1_{\gamma\gamma}^{ab}$ (corresponds to the interaction of angles, γ , having one $\text{Si}-\text{Cl}$ side in common), and H_ϵ . The remaining constants are either equal or very close to the

Table 1. Vibrational Spectrum of the Molecules $(\text{CH}_3)_3\text{SiX}$ ($\text{X}=\text{Cl}$, H ; Type A_1 ; Frequencies in cm^{-1})

Interpretation*	Experimental frequencies**				Calculated frequencies***	Forms of the vibrations****							
	according to ref. 5	IR (ref. 3) (l)	Ram. (ref. 3) (l)	Ram. (ref. 6)***		$q(-)$	$q(+)$	$\alpha(-)$	$\alpha(+)$	β	Q	q'	s
$\nu(\text{CH}_3)(-)$	2977	2969	2970	2969	2977 2968	1 1	-0.709 -0.709	-0.052 -0.051	0.072 0.072	0.056 0.056	0.001 0.001	-0.002 -0.012	0.060 0.060
$\nu(\text{CH}_3)(+)$	2912	2911	2906	2900	2908 2898	0.709 0.709	1 1	-0.040 -0.040	-0.028 -0.028	0.040 0.040	-0.059 -0.059	0.001 0.002	0.001 0.001
$\delta(\text{CH}_3)(-)$	1415	1414	1414	1416	1414 1425	-0.040 -0.041	0.027 0.028	1 1	-1.365 -1.407	0.219 0.240	-0.004 -0.005	0.040 -0.015	-0.031 -0.032
$\delta(\text{CH}_3)(+)$	1260	1248	1263	1256	1259 1260	-0.035 -0.036	-0.050 -0.051	1.388 1.411	1 1	-1.419 -1.426	0.214 0.218	-0.005 0.003	-0.007 -0.009
$\rho(\text{CH}_3)$	767	848	852	852	870 874	0.066 0.068	-0.051 -0.052	-0.282 -0.288	0.453 0.470	1 1	-0.109 -0.088	0.145 0.016	0.253 0.226
$\nu(\text{SiCl}_3)$	640	—	639	637	635 629	0.038 0.030	0.007 0.016	-0.157 -0.144	0.058 -0.004	0.431 0.302	1 0	-0.483 -0.178	-0.264 -0.178
$\nu(\text{Si}-\text{X})$	487	—	467	469	474 2118	-0.010 0.607	0.022 -0.006	0.038 0.012	-0.096 0.027	-0.205 -0.021	0.385 -0.021	1 1	0.430 0.029
$\delta(\text{SiCl}_3)$	242	—	242	239	244 222	-0.026 -0.018	0.017 0.011	0.121 0.094	-0.090 -0.043	-0.240 -0.193	-0.034 0.002	-0.115 0.130	1 1

*Vibrations: ν - stretching; δ - deformation; ρ - rocking; (+) - symmetric; (-) - asymmetric.

**IR - infrared spectrum; Ram. - Raman spectrum; l - liquid.

***Our interpretation.

****In each line, the upper numbers refer to $(\text{CH}_3)_3\text{SiCl}$, the lower to $(\text{CH}_3)_3\text{SiH}$.

responding quantities in dimethyldichlorosilane and trimethylsilane. The following set (in 10^6 cm^{-2}) was chosen:

The standard symbols (see refs. 7, 8, and 10) are used.

$$K_Q = 5.077, \quad k_{s(1)}(\text{Si}-\text{Cl}) = 4.000, \quad k_{s(2)}(\text{C}-\text{H}) = 8.100,$$

$$k_\alpha = 0.672, \quad k_\beta = 0.655, \quad k_\gamma = 1.247, \quad k_\epsilon = 0.845,$$

$$h_\alpha = 0.070, \quad a = 0.350, \quad A = A_\beta - B_\alpha = 0.270,$$

$$l_{\alpha\alpha} = l_{\beta\beta} = -0.035, \quad l_{\beta\beta} = -0.030, \quad H_\gamma = 0.080,$$

$$a' = a_\gamma - b_\epsilon = 0.290, \quad m_{\beta\gamma} = -0.023, \quad n_{\beta\gamma} = -0.010,$$

$$l_{\gamma\gamma}^{ab} = 0.314, \quad m_{\beta\epsilon} = 0.080, \quad n_{\beta\epsilon} = -0.010, \quad H_\epsilon = -0.203,$$

$$m_{\gamma\epsilon} = 0.237, \quad l_{\alpha\epsilon} = 0.075, \quad A_\epsilon - B_\epsilon = A_\gamma - B_\epsilon = A_\gamma - B_\gamma = 0.350.$$

DISCUSSION OF THE RESULTS

Application of the potential constants thus obtained to the calculation of the vibration frequencies gave satis-

Table 2. Vibrational Spectrum of the Molecules $(\text{CH}_3)_3\text{SiX}$ ($\text{X}=\text{Cl}$, H ; Type A_2 ; Frequencies in cm^{-1})

Interpretation*	Calculated frequencies***	Forms of the vibrations****		
		q	α	β
$\nu(\text{CH}_3)(-)$. . .	2976 2966	1 1	0.072 0.071	-0.079 -0.080
$\delta(\text{CH}_3)(-)$. . .	1413 1422	0.029 0.029	1 1	0.235 0.238
$\rho(\text{CH}_3)(+)$. . .	820 835	-0.049 -0.049	-0.295 -0.303	1 1

*, **** See Table 1.

factory results: the maximum deviations of the calculated frequency values from those observed amount to $15\text{--}25 \text{ cm}^{-1}$ for $\rho(\text{CH}_3)$ and to about 15 cm^{-1} for $\delta(\text{SiCl}_3)$ (type E) and $\delta(\text{Si}-\text{Cl})$; for the remaining frequencies, there is practically complete coincidence.

Basically, the calculations confirm the vibrational interpretation carried out by Smith.⁵ The vibrations

Table 3. Vibrational Spectrum of the Molecules $(\text{CH}_3)_3\text{SiX}$ ($\text{X}=\text{Cl}$, H ; Type E; Frequencies in cm^{-1})

Interpretation*	Experimental frequencies**				Calculated frequencies***	Forms of the vibrations****											
	according to ref. 5	IR (ref. 3) (l)	Ram. (ref. 3) (l)	Ram. (ref. 6)***		q	q^a	q^b	α	α^a	α^b	β^a	β^b	Q	s	τ	
$\nu(\text{CH}_3)(-)$. . .	2977	2969	2970	2969	2976 2967	1 1	0.282 0.461	-0.703 -0.702	0.072 0.071	0.020 0.033	-0.052 -0.051	-0.022 -0.036	0.057 0.057	-0.001 -0.001	-0.010 0.003	-0.060 -0.066	
$\nu(\text{CH}_3)(+)$. . .	2977	2969	2970	2969	2977 2967	-0.195 -0.311	1 1	0.142 0.223	-0.014 -0.022	0.072 0.072	-0.080 0.016	-0.011 -0.081	-0.001 -0.018	0.080 0.084	0.080 0.021		
$\nu(\text{CH}_3)(+)$. . .	2912	2911	2906	2900	2908 2899	0.704 0.704	-0.005 -0.004	1 1	-0.029 -0.028	0 0	-0.040 -0.039	0.002 0.001	-0.040 0.039	-0.060 -0.059	-0.001 -0.001		
$\delta(\text{CH}_3)(-)$. . .	1454	1454	1449	1416	1413 1423	0.029 0	0.029 0.029	-0.020 -0.001	0.985 0.013	1 1	-0.696 -0.006	0.242 0.241	-0.164 -0.005	0.015 0.006	0.024 0.004		
$\delta(\text{CH}_3)(+)$. . .	1454	1454	1449	1416	1414 1426	0.029 0.029	0.006 0.023	-0.021 -0.021	1 1	0.204 0.803	-0.685 -0.705	0.051 0.196	-0.172 -0.163	-0.002 -0.008	-0.009 0.009	-0.027 -0.042	
$\delta(\text{CH}_3)(+)$. . .	1260	1248	1263	1256	1263 1247	-0.024 -0.025	0.001 0	-0.036 -0.037	0.732 0.731	0.012 0	1 1	-0.007 0.003	-1.015 -1.021	0.166 0.151	0.007 0	-0.004 0.086	
$\nu(\text{CH}_3)(-)$. . .	857	848	852	852	880 872	-0.008 0.013	-0.046 -0.047	-0.002 -0.016	-0.004 0.135	-0.306 -0.305	0.046 -0.019	1 1	-0.082 0.241	-0.192 -0.096	-0.203 -0.183	-0.090 -0.526	
$\rho(\text{CH}_3)(-)$. . .	857	848	852	852	826 835	0.069 0.073	-0.009 0.015	-0.046 -0.044	0.408 0.391	-0.057 0.092	-0.293 -0.363	0.226 -0.267	1 1	0.077 0.080	-0.068 -0.014	-0.159 0.701	
$\nu(\text{SiCl}_3)(-)$. . .	700	762	757	762	759 714	0 0.006	-0.067 -0.032	0.043 0.027	-0.219 -0.081	-0.319 -0.176	-0.056 -0.007	1.302 0.750	-0.153 -0.080	1 1	0.128 0.209	-0.245 -0.245	
$\delta(\text{SiCl}_3)(-)$. . .	330	—	242	239	257 244	-0.007 0.005	-0.027 -0.023	-0.001 -0.005	0 0.020	-0.115 -0.092	0.062 -0.022	0.377 0.306	-0.043 0.057	0.017 0.006	1 1	-0.868 0.117	
$\delta(\text{Si}-\text{X})$. . .	188	—	188	187	173 914	0.013 -0.009	-0.019 -0.033	-0.006 0.011	0.024 -0.122	-0.068 -0.226	-0.077 -0.032	0.275 0.730	0.123 -0.164	0.011 -0.125	1.124 -0.147	1 1	

*, **** See Table 1.

$\rho_{A_1}(\text{CH}_3)$, $\delta_E(\text{CH}_3)(-)$, $\nu_E(\text{SiC}_3)(-)$, and $\delta_E(\text{SiC}_3)(-)$ constitute an exception. The frequency lying in the 850-860 cm^{-1} region must be identified with the vibration $\rho_{A_1}(\text{CH}_3)$ which corresponds to rocking of the methyl group. The frequency $\sim 760 \text{ cm}^{-1}$ is related to stretching of the Si-C bond [$\nu_E(\text{SiC}_3)$]. The latter agrees with the conclusion of ref. 4. The frequencies $\sim 1415 \text{ cm}^{-1}$ must be assigned to the asymmetric deformation vibrations $\delta_E(\text{CH}_3)$. During the transition from CH_3SiCl_3 to $(\text{CH}_3)_4\text{Si}$, they vary within the limits of 1400-1430 cm^{-1} . The band $\sim 1450 \text{ cm}^{-1}$ is very weak and may be represented as a combination of 1260 and 188 cm^{-1} . The frequency of the skeletal deformation vibration $\delta_E(\text{SiC}_3)$ lies in the region 240-250 cm^{-1} , not 330 cm^{-1} . The 330 cm^{-1} line is possibly a combination [$\delta(\text{Si-Cl})$ and a torsional vibration] or belongs to an impurity. It was not observed by Batuev et al.⁶ in the Raman spectrum.

Our assignment also agrees [except for $\delta_E(\text{CH}_3)(-)$] with the recently published theoretical conclusions of Shimizu and Murata.³

Comparison of the force constants for the molecules of the series under consideration shows a certain regular progression in their variation (similar to the variation in intensities⁴) as the methyl groups are replaced by chlorine atoms.

For example, for the diagonal constants:

	$(\text{CH}_3)_4\text{Si}$	$(\text{CH}_3)_3\text{SiCl}$	$(\text{CH}_3)_2\text{SiCl}_2$	CH_3SiCl_3
$K_0(\text{Si-C})$	4.62	5.077	5.247	5.290
$k_{q(1)}(\text{Si-Cl})$	—	4.000	4.240	4.527
$k_{q(2)}(\text{C-H})$	8.050	8.100	8.143	8.153
$k_a(\text{HCH})$	0.675	0.672	0.670	0.665
$k_3(\text{HCSi})$	0.660	0.655	0.650	0.640
$k_2(\text{ClSiCl})$	—	—	1.160	1.307
$k_7(\text{ClSiC})$	—	1.247	1.283	0.986
$k_2(\text{CSiC})$	0.856	0.845	0.840	—

Accumulation of chlorine atoms on silicon leads to an increase in the stiffness of the adjacent Si-C bonds and of the Si-Cl bonds themselves; and to an increase in the polarity of the C-H bonds.⁶ Furthermore, comparison shows that the Si-C bond in the methylsilane molecules is about 10% weaker than in the corresponding chloro derivatives.

The values of the coefficients k_α and k_β diminish systematically during the transitions $\text{CH}_3\text{SiH}_3 \rightarrow (\text{CH}_3)_4\text{Si} \rightarrow \text{CH}_3\text{SiCl}_3$. The stiffness of the HCH and HCSi angles diminishes.

The forms of the normal vibrations of trimethylsilane have also been calculated in the present work. A comparison of the frequency and form values obtained

for $(\text{CH}_3)_3\text{SiCl}$ and $(\text{CH}_3)_3\text{SiH}$ is made in Tables 1-3. The analysis shows that the $\nu(\text{CH}_3)$ symmetric stretching vibrations are entirely characteristic both in frequency and in form: the frequencies differ only within the limits of 10 cm^{-1} ; the form coefficients are identical. The same may also be said about the corresponding asymmetric vibration of type A_1 . For the $\nu(\text{CH}_3)$ asymmetric vibrations of type E which are related to the stretching of C-H bonds, the amplitudes of the changes in the length of the other C-H bonds (the other group of equivalent coordinates) and in the corresponding HCH and HCSi angles are about 1.5 times as large in the trimethylsilane molecule as in $(\text{CH}_3)_3\text{SiCl}$.

The vibrations $\delta(\text{CH}_3)(+)$, $\delta(\text{CH}_3)(-)$, and $\rho(\text{CH}_3)$ of type A_1 and $\rho(\text{CH}_3)(+)$ of type E are also quite characteristic both in frequency and in form: there exists a difference only in the amplitudes of the change in the Si-X lengths and in the values of the CSiC and CSiX angles. For the $\delta_E(\text{CH}_3)$ and $\rho_E(\text{CH}_3)$ asymmetric vibrations, the ratios between the form coefficients are analogous (to a somewhat grosser approximation) to those which exist for $\nu_E(\text{CH}_3)(-)$. The character of the vibration of the molecular skeleton changes substantially on going from $(\text{CH}_3)_3\text{SiH}$ to $(\text{CH}_3)_3\text{SiCl}$.

REFERENCES

1. H. Kriegsmann, Z. anorg. u. allgem. Chem. **299**, 130 (1959).
2. K. Shimizu and H. Murata, Bull. Chem. Soc. Japan **32**, No. 1, 46 (1959).
3. K. Shimizu and H. Murata, J. Mol. Spectroscopy **4**, 201-213, 214-223 (1960).
4. L. A. Ignat'eva, P. A. Bazhulin, and I. K. Baeva, Vestnik. Moskov. Gosudarst. Univ., Ser. Mat., Mekhan., Astron., Fiz. Khim. **6**, 127 (1959).
5. A. L. Smith, J. Chem. Phys. **21**, 1997 (1953).
6. M. I. Batuev, V. A. Ponomarenko, A. D. Matveeva, and A. D. Snegova, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk **8**, 996 (1958).
7. I. F. Kovalev, Opt. i Spekt. **8**, 315 (1960), Optics and Spectroscopy **8**, 166 (1960).
8. M. V. Vol'kenshtein, M. A. El'yashevich, and B. I. Stepanov, "Molecular Vibrations," Vol. 1 Gosudarst. Izd. Tekh. i Teoret. Lit., Moscow, 1949.
9. L. S. Mayants, Trudy Fiz. Inst. Akad. Nauk SSSR **5**, 65 (1956); Doklady Akad. Nauk SSSR **89**, 423 (1953).
10. I. F. Kovalev, Opt. i Spekt. **8**, 594 (1959), Optics and Spectroscopy **6**, 387 (1959).

TEMPERATURE DEPENDENCE OF LINE WIDTH IN THE RAMAN SPECTRA OF CRYSTALLINE SUBSTANCES

A. V. Rakov (pp. 713-716)

Received 8 July 1960

The effect of the rotation of molecules in the crystalline lattice on the broadening of Raman lines was investigated. The variation in line-width was studied in a number of polycrystalline substances at different temperatures: p-dichlorobenzene in the interval +52 to -150°C, p-xylene in the interval -5 to -80°C, and cyclohexane in the interval 0 to -90°C. The axes of rotation of molecules in the lattice and the heights of the corresponding potential barriers were determined.

In a previous communication¹ it was shown that the random process of rotation of molecules in the liquid state exerts a substantial effect on line-width in Raman spectra. A number of experimental results indicate that random rotations of molecules also occur in the crystalline state.² In connection with this it was of interest to investigate the influence of the rotation of molecules on line-width in Raman spectra.

It must be noted first of all that, relative to the liquid state, the crystalline lattice will affect substantially the nature of the random rotations of molecules. In the liquid state, the molecule can rotate freely about any axis, while in a crystal the rotation of a molecule can not violate the symmetry of the crystalline lattice. Hence it follows that, in the crystalline lattice, the rotation of molecules can occur only relative to their axes of symmetry. At the same time, the probability of rotation of a molecule about different axes might be different.

According to ref. 1, random rotation of molecules leads to additional broadening of the depolarized lines ($\rho \approx 6/7$) by a factor $\Delta\omega = 1/\tau_0$, where τ_0 is the half-width of the correlation function for the given random process. Usually τ is called the average time of rotation of the molecule, or the relaxation time. Since the processes of rotation in the crystalline state are different from those in the liquid state the τ_0 will be different in the two states. Hence it must be expected that a discontinuous transition would occur in the measured width of depolarized lines in going from the liquid to the crystalline state. This effect has been observed for several substances and has been described by us^{3,4} as well as by other authors.⁵

Of particular interest is the case when the molecule in the crystalline lattice can rotate only about a single axis. Such a case would occur either when the molecule has only one symmetry axis or when the probability of rotation about one of the several symmetry axes is much greater than for the other possible rotations. In such a case, if the induced moment of some molecular vibration, whose tensor of polarization derivative possesses an anisotropic part, happens to coincide with the direction of the axis of rotation, then the width of the line corresponding to this vibration, according to ref. 1, will be independent of the temperature of the crystal. At the same time it does not matter whether the substance under investigation is monocrystalline or polycrystalline.

The following rule is obtained as the result of the foregoing considerations and of the theoretical representations of ref. 1: The presence of at least one depolarized line whose line-width is independent of temperature, among depolarized lines whose line-widths are tempera-

ture-dependent, in the Raman spectrum of a crystalline substance, indicates that the most likely rotation of the molecule in the crystalline lattice is the one relative to a single axis.

It must be noted that for any molecule, in the case of in-plane depolarized vibrations of the same symmetry class, the induced moments will have the same direction. Whence it follows that the line-widths of these vibrations must be either dependent on the temperature of the crystal or independent (coincidence and divergence, respectively, of the direction of the induced moments with the rotation axis). Assuming the exciting electrical field to be spherical under the experimental conditions, it can be shown that in the case of coincidence between the direction of the induced moments of in-plane depolarized vibrations and the rotation axis, the main axes of the ellipsoid of the derivative of the polarization tensor must intersect the rotation axis at an angle of about 45°.

As has been pointed out before, there occurs a discontinuity in the magnitude of τ_0 which depends on the height of the potential barrier for rotation of the molecule in going from the liquid phase to the crystalline phase. In relation to this, it was of interest to follow the variation in the magnitude of the potential barrier U with the phase transition. In the crystalline state the magnitude of U is related to the line-width δ by the relation analogous to the one derived in ref. 1:

$$\delta(T) \approx \Delta^0 + A \exp\left(-\frac{U}{RT}\right),$$

where Δ^0 is a constant, A is a normalizing factor, R is the gas constant, and T is the absolute temperature.

We chose p-dichlorobenzene (m.p. = +52.7°C), p-xylene (m.p. = +13.2°C), and cyclohexane (m.p. = +6.5°C) as the objects of our investigation. These substances were studied in the polycrystalline state. The widths of lines with different degree of depolarization ρ in the spectra of all three substances were measured over a wide temperature interval. As a result of the measurements, it was determined that the widths of lines possessing low values of ρ were almost temperature-independent, in accordance with ref. 1. The widths of depolarized lines did not all vary in the same way with temperature. The results of measurements of widths of lines of $\rho \approx 6/7$ are shown in Table 1.

Let us examine the results obtained for each substance separately.

p-Dichlorobenzene. As can be seen from Table 1 the widths of the two depolarized lines at 307 and 627 cm^{-1} do not depend on the temperature of the crystal, while the width of the line at 1578 cm^{-1} is temperature-dependent.

Table 1

Substance	$\Delta\nu$ (cm^{-1})	ρ^{**}	True line-width (cm^{-1})				
			+52° C	+33° C	0° C	-80° C	-150° C
P-Dichloro- benzene	307 *	dp	1.0±0.5	1.1±0.5	1.0±0.5	1.2±0.5	1.0±0.5
	627 *	dp	1.0±0.5	1.0±0.5	0.8±0.5	0.8±0.5	1.0±0.5
	1578	0.6	4.0±0.3	3.5±0.3	2.8±0.3	1.8±0.3	1.5±0.3
p-Xylene	$\Delta\nu$	ρ	-5° C	-25° C	-45° C	-65° C	80° C
	645 *	0.89	1.1±0.5	1.1±0.05	1.2±0.5	1.1±0.5	1.0±0.5
	1618	0.72	3.8±0.3	3.0±0.3	2.6±0.3	2.1±0.3	2.0±0.3
Cyclohexane	$\Delta\nu$	ρ	0° C	-25° C	-45° C	-65° C	-80° C
	1029	0.79	7.2±0.4	5.0±0.4	3.6±0.4	2.1±0.4	1.0±0.4
	1267	0.77	11.7±0.4	—	5.0±0.5	—	1.0±0.4
	1445	0.81	10.6±0.3	—	5.0±0.5	—	1.7±0.3

*The errors shown in the table comprise the errors in the measurement of line-widths as well as the errors incurred in calculating the true line-widths from the observed contour was about 10%.

**The designation dp means depolarized line.

According to the foregoing considerations, these results indicate that the most probable rotation of a molecule of p-dichlorobenzene in the crystalline lattice is about a single axis. The molecule of p-dichlorobenzene belongs to the point symmetry group $V_h \equiv D_{2h}$ and has three second-order symmetry axes. Both depolarized lines whose widths are temperature-independent belong to the in-plane vibrations of symmetry B_{1g} , thus substantiating the above-mentioned rule for in-plane depolarized vibrations. According to the foregoing considerations, rotation about the symmetry axis perpendicular to the plane of the benzene ring can not occur. Unhappily, it is not possible to determine relative to which of the two axes lying in the plane of the molecule are the induced moments of these vibrations directed. It can be proposed that the axis of rotation is the symmetry axis passing through the chlorine atoms since the moment of inertia of the molecule relative to this axis is smaller by almost an order of magnitude than the moment of inertia relative to the second axis lying in the plane of the benzene ring.

p-Xylene. There exists one depolarized line at 645 cm^{-1} in the spectrum of p-xylene whose width is temperature-independent. The widths of two other lines (1618 and 3012 cm^{-1}) are temperature-dependent. These results indicate that the most probable rotation of a molecule of p-xylene in the crystalline lattice is the one relative to a single axis. The assignment of the molecule of p-xylene to a definite point symmetry group is complicated by the lack of precise data about the position of the methyl groups. Usually it is assigned to the C_{2h} or C_{2v} groups. The results of the present investigation provide additional evidence for deciding which of the two alternatives is the more probable one. The line at 645 cm^{-1} , whose width is temperature-independent, corresponds to an in-plane vibration. This follows from the degeneracy of the symmetry classes of vibrations in going from benzene to p-xylene. Hence the induced moment of the vibration lies in the plane of the benzene ring. If p-xylene belongs to the point symmetry group C_{2h} then the molecule has only one symmetry axis of the second order perpendicular to the benzene ring. Then rotation about this axis will, according to the foregoing discussion, lead to the temperature-dependence of the width of the 645 cm^{-1} line. Thus the experimental results do not agree with

the molecular model for p-xylene based on the symmetry group C_{2h} .

In the case of the C_{2v} symmetry group, the p-xylene molecule has one symmetry axis of the second order which lies in the plane of the benzene ring and perpendicular to the axis passing through the carbon atoms of the methyl groups. Rotation of the molecule about this axis does not contradict the experimental results and it follows that the induced moment of the vibration 645 cm^{-1} is directed along this axis. It must be noted also that in the case of C_{2h} symmetry some of the transitions must be infrared-inactive while the opposite should occur in the case of C_{2v} symmetry. Comparison of Raman spectra with infrared spectra indicated that no lines were infrared-inactive.

Cyclohexane. The cyclohexane molecule belongs to the D_{3d} point symmetry group and has one third-order symmetry axis and three second-order symmetry axes. The absence of intense depolarized lines whose widths would be temperature-independent in the spectra of crystalline cyclohexane did not permit the ascertainment of the rotation axes. Hence another possibility was used to determine the latter.

The nuclear magnetic resonance spectrum of crystalline cyclohexane has been investigated.⁶ The authors have shown that in the temperature interval from -87 to $+6.5^\circ\text{C}$ the molecules of cyclohexane rotate about second order symmetry axes. Using the results of this investigation in the given temperature interval, we evaluated the height of the potential barrier associated with the rotation of cyclohexane to be $2 \pm 1 \text{ kcal/mole}$. Our own results also permit the calculation of the height of the potential barrier associated with the rotation of cyclohexane in the same temperature interval. The calculated value is $2.8 \pm 0.5 \text{ kcal/mole}$. It is easily seen that our value for the height of the potential barrier agrees with the one calculated on the basis of the results of the investigation in ref. 6. Hence it follows that the widths of the lines investigated in the spectrum of crystalline cyclohexane ($\Delta\nu = 1029, 1267$, and 1445 cm^{-1}), are mainly determined by the rotations of molecules in the lattice about their second-order symmetry axes.

The heights of the potential barriers associated with the rotation of molecules in the crystalline lattices of the other substances were calculated from the results of the present investigation. The results of the calculations are shown in Table 2, which also shows the magnitudes of the potential barriers for rotation of p-xylene and cyclohexane in the liquid state.*

*The results of the investigation in ref. 5 were used in the calculation of the heights of the potential barriers for the rotation of p-xylene and cyclohexane molecules in the liquid phase.

Table 2

Substance	Height of the potential barrier (kcal/mole)	
	Crystalline phase	Liquid phase
p-Dichlorobenzene.....	2.2 ± 0.5	—
p-Xylene	3.0 ± 0.5	2.2 ± 0.5
Cyclohexane	2.8 ± 0.5	2.8 ± 0.5

It can be seen from Table 2 that, within experimental error, the heights of the potential barriers for rotation of the molecules of the three substances investigated in the crystalline and liquid phases do not differ very much from each other.

The experimental results obtained in the present investigation show that the investigation of the temperature dependence of the line-widths in Raman spectra of crystals can give, in a number of cases, important data on the kinetics of molecules in the lattice, on the symmetry of molecules, and on the directions of the main

axes of the ellipsoid of the derivative of the polarization.

In conclusion the author would like to indicate his gratitude to P. A. Bazhulin for his valuable advice concerning the present investigation and his constant interest in its progress.

REFERENCES

1. A. V. Rakov, Opt. i Spekt. 7, 202 (1959), Optics and Spectroscopy 7, 128 (1959).
2. A. Andrew, "Nuclear Magnetic Resonance." Izd. Inostrannaya Lit., Moscow, 1957. Cambridge Univ. Press, 1956.
3. P. A. Bazhulin and A. V. Rakov, Doklady Akad. Nauk SSSR 105, 54 (1955).
4. A. V. Rakov, Proc. Tenth Conf. Spectroscopy, Lvov, 1957, vol. 1, p. 229.
5. N. I. Rezaev, Proc. Tenth Conf. Spectroscopy, Lvov, 1957, vol. 1, p. 230.
6. E. R. Andrew and R. G. Eades, Proc. Roy. Soc. A216, 398 (1953).

UNIVERSAL MOLECULAR INTERACTIONS AND THEIR EFFECT ON THE POSITION OF THE ELECTRONIC SPECTRA OF MOLECULES IN TWO-COMPONENT SOLUTIONS

I. Theory (Liquid Solutions)

N. G. Bakhshiev (pp. 717-720)

Received 4 July 1960

Starting from the most general physical considerations, a simple theory was developed describing the effect of universal intermolecular interactions (orientation, induction, and dynamic effects) on the position of the electronic spectra of molecules in two-component liquid solutions. Using the Onsager-Böttcher model of the structure of solutions, new and simple expressions were found correlating the magnitude of the spectral shift with physical characteristics of the solvent and the molecules of the solute. The effect of dispersive interactions on the position of the spectra is reviewed.

1. In recent years, considerable progress has been made in understanding the effect of the solvent on various spectral characteristics of the solute molecule. In refs. 1-3 quantum-mechanical methods were used to obtain general theoretical expressions linking the magnitude of the spectral shift accompanying the vapor-solution transition to the basic characteristics of the solute molecules and the solvent. It is regrettable that these expressions are unsuitable for direct quantitative experimental verification, due to their complexity and the presence of a large number of unevaluated parameters. This compelled the authors¹⁻³ to introduce models of the molecule-solvent system investigated. For this purpose, representations of the solution structure models were borrowed from the theory of the polarization of liquid dielectrics (Onsager's model⁴ in particular). This made it possible to establish relationships between the spectral shift and the generalized physical properties of the solvent such as the dielectric constant and the index of refraction. Nevertheless, the final theoretical relationships remained very cumbersome.

From the analysis of these relationships in refs. 5-7, a relatively simple expression for the magnitude of the shift of spectra was obtained. This expression permitted direct comparison with experiment and was found to be in satisfactory quantitative agreement with the experimental data. Later, in ref. 8, it was proposed to subdivide the intermolecular interactions in solutions into universal interactions, associated with the collective effect of the entire surrounding set of solvent molecules on the mole-

cule under investigation, and specific interactions, produced by the individual interactions of the molecule in question with one or more of the particles of the surrounding medium. It was shown that theoretical considerations allow consideration of the universal effect of the solvent as a physical dielectric medium in general form. This effect is determined by the magnitude of the solution's internal field.¹⁻⁷

Proceeding from quite general physical considerations, it is not difficult to show that the universal effect of the internal field of a solution on the spectra of the dissolved molecules can be calculated by methods which are simpler than those used in refs. 1-3. In connection with this, we emphasize that despite the complexity and cumbersomeness of the expressions obtained in refs. 1-3, a number of very important factors were not taken into account in deriving them. No consideration was given to the change of some electric properties of a molecule when it is dissolved and excited, or what is more important, to the nonparallelism of the permanent dipole moments of the particles under investigation in the ground and excited electronic states.

From the above considerations, an attempt is made in this paper to construct a simple and at the same time fairly general theory which takes account of the universal effect of internal field (orientation, induction and dynamic effects), and also the effect of dispersive interactions on the position of electronic spectra of molecules in liquid two-component solutions (i.e., including two kinds of molecules—solute and solvent). A broad quanti-

tative comparison of this theory with experiment and with other treatments¹⁻⁷ is also attempted.

2. Let us consider an isolated molecule of the substance under investigation. This molecule can be in one of two electronic energy states, the ground (g) or excited (e) state, having energies E_g and E_e respectively (Fig. 1,a).

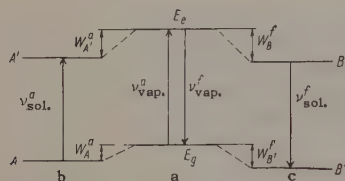


Fig. 1. Diagram of the electron levels of a molecule as a vapor and in solution. a—absorption and fluorescence (vapor); b—absorption (solution); c—fluorescence (solution).

In the absorption or emission of a quantum of frequency $\nu = (E_e - E_g)/h$, a redistribution of electron density takes place. In the first case, the permanent dipole moment changes from μ_g to μ_e , and in the second, from μ_e to μ_g (μ_g and μ_e are the dipole moments of the molecule in the ground and excited states, respectively). It should be noted that, in general, the moments μ_g and μ_e are not parallel, but are at an angle α with respect to each other (see Fig. 2,a).

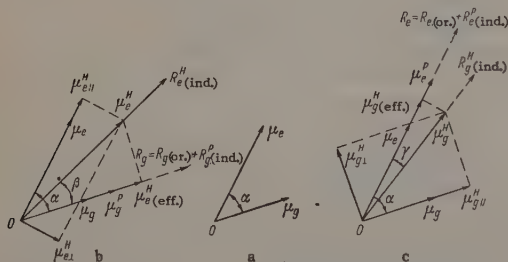


Fig. 2. Calculation of the dipole moments of a solute molecule in the equilibrium and non-equilibrium electronic states. For a, b, c, refer to the subscript of Fig. 1.

When the molecule under investigation is mixed with the solvent, it interacts with the entire surrounding set of dielectric molecules. This changes a number of its electrical and optical properties, particularly the position of its electronic levels, by the value of the so-called energy of stabilization W_i .⁹ This change in position appears as a shift of the spectra.*

*Here we are not investigating the effect of specific interactions⁹ due to the chemical nature or structural peculiarities of the solute and solvent molecules.

It should be kept in mind that the properties of the dissolved molecule-solvent system differ substantially from the properties of an isolated molecule. This is immediately evident from the fact that the concept of two electron levels, ground and excited, is not sufficient to describe the energy state of this system (Fig. 1,a). For each electronic state of the solute molecule, it is necessary to consider two levels—the equilibrium and

nonequilibrium* (or so-called Franck-Condon levels.^{2,6,11}

*Special mention should be made of the fact that Ne-porent¹⁰ arrived at similar conclusions on the basis of an analysis of intramolecular processes. He proposed a new scheme of four electronic levels (two equilibrium and two nonequilibrium) for a given group of molecules.

This is explained as follows: First, the configuration of the solvent molecules surrounding a solute molecule, which is in the ground equilibrium state, is in general different from the configuration for the excited equilibrium state.* Secondly, according to the Franck-Condon

*It is known that the rotational relaxation time τ' of the molecules of a liquid (the solvent) is 10^{-10} – 10^{-11} sec at room temperature,¹² while the duration of the excited state τ_{fl} of organic molecules is about 10^{-8} sec (i.e., $\tau' \ll \tau_{fl}$). Some particular cases in which $\tau' \approx \tau_{fl}$ or $\tau' \gg \tau_{fl}$ will be investigated separately.

principle, this configuration does not change during the process of electron transition. In other words (Fig. 1,b,c), the level stabilization energies A and A' (for absorption) and B and B' (for emission) are determined by different configurations of the solvent molecules, corresponding to the initial ground and excited equilibrium states of the solute molecule (A and B correspond to the ground and excited equilibrium levels, and B' and A' to the ground and excited nonequilibrium levels).

The mean energy W_i of interaction of the dissolved molecule with the medium* obviously is determined by

*Here we are considering molecules which are not charged and exist in dilute solution (concentration less than 10^{-3} mole/liter), so that interaction among the particles of the solute can be neglected.

the value of its dipole* moment μ_i (representing the sum

*Higher order moments are not investigated here.

of the permanent moment and the moment induced by the light wave) in the corresponding state, and by the value of some effective field F_i acting on the molecule in solution and equivalent to the over-all influence of the entire set of solvent particles. In addition to this,

$$W_i = -\mu_i F_i \cos \alpha_i = -\mu_{i,eff} F_i, \quad (1)$$

where α_i is the angle between the direction of the corresponding dipole and the field interacting with it.

In the general case, the field F_i is composed of two parts⁶: the permanent field F'_i , determined by the permanent and static induced dipole moments which are present in the solute and solvent molecules, and the variable field F''_i , which is produced by the polarization of the medium caused by the induced moment of the molecule under investigation. The latter moment is in turn induced by a light wave. It is expedient to study these cases separately.

Orientation-Induction Shift. The field F'_i is in turn composed of two parts: the field $F'_{i,or}$ associated with the orientation of the solvent molecules surrounding the molecule under investigation, and the field $F'_{i,ind}$ determined by the inductive polarization of the dielectric. Therefore, it has to be kept in mind that the field $F'_{i,or}$, in accordance with the Franck-Condon principle, is determined by the initial equilibrium state of the molecule, i.e., for absorption by the ground state and for emission by the excited state (for $\tau' \ll \tau_{fl}$). The inductive part

the field (F'_{ind}) at any given moment depends on the corresponding values of the dipole moments and the polarizability of the solute and solvent molecules.

The difference in energies of stabilization $\Delta W'$ of the ground and excited electronic levels, which determines the magnitude of the shift of the corresponding spectrum (Fig. 1,b,c), is equal, as can easily be shown, to the work done by the field F'_i in changing the dipole moment of the molecule from its initial to its final value; i.e., for absorption

$$\Delta W'_{or.} = - \int_{\mu_g^{(eff.)}}^{\mu_e^{(eff.)}} F_{g(or.)} d\mu; \quad \Delta W'_{ind.} = - \int_{\mu_g^{(eff.)}}^{\mu_e^{(eff.)}} F_{ind.} d\mu \quad (2)$$

and for emission

$$\Delta W'^f_{or.} = - \int_{\mu_g^{(eff.)}}^{\mu_e^{(eff.)}} F_{e(or.)} d\mu; \quad \Delta W'^f_{ind.} = - \int_{\mu_g^{(eff.)}}^{\mu_e^{(eff.)}} F_{ind.} d\mu. \quad (3)$$

μ_g^P and μ_e^P are the dipole moments of the solute molecule in equilibrium, and μ_g^H and μ_e^H are the dipole moments in the Franck-Condon states, where g corresponds to the ground state and e to the excited state ($\mu_g^{H(eff.)}$ and $\mu_e^{H(eff.)}$ are the projections of the moments μ_g^H and μ_e^H in the direction of the corresponding field $F_{i(or.)}$). Therefore, the magnitude of the spectral shift for absorption or fluorescence, as determined by the interaction of permanent and static induced dipoles, will be written in the following form

$$\Delta\nu'^f = \frac{\Delta W'^f_{or.} + \Delta W'^f_{ind.}}{hc} = \Delta\nu'^f_{or.} + \Delta\nu'^f_{ind.} \quad (4)$$

Dynamic Shift. In the same way, the expression for the difference of stabilization energies, as determined by the influence of the field $F''_{dyn.}$ (which we will call dynamic), can be written in the form⁶

$$\Delta W''_{dyn.} = - \int_0^{P_0} F''_{dyn.} dP, \quad (5)$$

where P_0 is the dipole moment associated with the electronic transition between the g and e states.

The total spectral shift caused by the transition from vapor to solution will be

$$\Delta\nu''^f = \Delta\nu'^f_{or.-ind.} + \Delta\nu''_{dyn.} = \frac{\Delta W'^f_{or.} + \Delta W'^f_{ind.} + W''_{dyn.}}{hc} \quad (6)$$

In general form, relationships (2)-(6) permit quantitative calculation of the universal effect of the internal field on the position of the spectra, using various models of the molecule-solvent system. In addition to this, we wish to point out that since only the electronic states of the molecule were considered above, expressions (2)-(6), strictly speaking, determine the frequency shift of purely electronic transitions. In the general case, these transitions are different for absorption and fluorescence spectra.

3. Let us investigate one particular case: using relationships (2)-(6), we will try to obtain expressions for the magnitude of the spectral shift in absorption and fluorescence, proceeding from Onsager's model of the molecule-solvent system.

It is appropriate at this point to briefly review the reasons for selecting the Onsager-Böttcher theory^{4,21} as

the basis for the model calculations, even though a number of better theories exist. There are several reasons, the most important being the relative simplicity, descriptiveness, and broad physical meaning of this theory, which contains a minimum number of parameters. As will be shown later, this makes possible the derivation of relatively simple and descriptive theoretical relationships which can be subjected to a thorough experimental check. Such an approach, motivated by a desire to explain the principles of the problem, appears to us to be fully justified. When we attempt to use more rigorous theories (Kirkwood,¹³ Froelich,¹⁴ Harris and Alder,¹⁵ Buckingham¹⁶), which take account of the correlation between the solute molecule and its nearest neighbors, it becomes necessary to introduce undetermined parameters whose presence excludes the possibility of a quantitative comparison of theory with experiment.

An aspect of Onsager's model which is very essential for the spectroscopic investigations is the fact that it is fully applicable to real molecules (see ref. 17) having any arbitrary spatial distribution of electrical charges and, consequently, has a much greater physical meaning than is usually assumed.¹⁸

In the Onsager-Böttcher theory, the part of the effective field F_i is played by the reaction field R_i ,¹⁴ which allows the molecule to act on itself through the surrounding medium. The expressions for the reaction fields R_g and R_e are written in the form

$$R_g = \frac{(\mu_g + \alpha R_g) 2\epsilon - 2}{r^3}; \quad R_e = \frac{(\mu_e + \alpha R_e) 2\epsilon - 2}{r^3} \quad (7)$$

where α is the mean static electronic polarizability of the molecule (assumed to be the same for the ground and the excited states),* ϵ is the static dielectric constant of

*For simplicity, we assume the polarizability α to be a scalar while still retaining the possibility of introducing necessary corrections. In the general case, the polarizability is characterized by a symmetrical tensor whose principal axes need not coincide with the direction of the permanent dipole moment of the molecule.

the medium (see below), and r is the Onsager cavity radius.

In connection with this, it is necessary to note that the static value ϵ can be used only when $\tau \gg \tau'$. The latter condition is usually fulfilled under experimental conditions (τ is the lifetime of the molecule in the appropriate electronic equilibrium state) for both the absorption and fluorescence spectra of liquid solutions. As seen in ref. 19, when fluorescence spectra are studied in the temperature range in which vitrification (or polymerization) of the solvent occurs, there is a sharp increase in the viscosity of the solvent, and, consequently, the relaxation time of the molecules of the solvent increases (if $\tau_{fl.} = \tau'$). Thus, the reorientation of solvent particles surrounding the excited molecule under investigation is not yet fully completed, and it is therefore necessary to use values of ϵ corresponding to higher frequencies (apparently $\omega = 2\pi/\tau_{fl.}$). The influence of relaxation effects produced by changes in the temperature and state of aggregation of the solvent (transition to solid solution, i.e., cases where $\tau' \approx \tau$ and $\tau' \gg \tau$) on the absorption and fluorescence spectra of the solute will be discussed in another paper.

Using formulas (7), it is not difficult to show that

$$R_{g(\text{or.})} = \frac{2\mu_g}{r^3} \left[\frac{\varepsilon' - 1}{2\varepsilon' \left(1 - \frac{\alpha}{r^3}\right) + 1 + 2\frac{\alpha}{r^3}} \right],$$

$$R_{s(\text{or.})} = \frac{2\mu_s}{r^3} \left[\frac{\varepsilon' - 1}{2\varepsilon' \left(1 - \frac{\alpha}{r^3}\right) + 1 + 2\frac{\alpha}{r^3}} \right], \quad (8)$$

where ε' is the contribution of the orientation polarizability of the solvent molecules to the magnitude of the dielectric constant. The value of the reaction field $R_{\text{ind.}}$ is determined at any given moment by

$$R_{\text{ind.}} = \frac{2\mu}{r^3} \left[\frac{n_0^2 - 1}{2n_0^2 \left(1 - \frac{\alpha}{r^3}\right) + 1 + 2\frac{\alpha}{r^3}} \right], \quad (9)$$

where n_0^2 is the component of the medium's dielectric constant as determined from the static electronic polarization of the dielectric. Finally, the reaction field $R_{\text{dyn.}}$, which is determined by the presence of the dipole moment P induced in the molecule by the light wave, can be written in the form²⁰

$$R_{\text{dyn.}} = \frac{2n_D^2 - 2}{2n_D^2 + 1} \cdot \frac{\alpha_{\text{dyn.}}}{r^3} E_{\text{eff.}} = \frac{2n_D^2 - 2}{2n_D^2 + 1} \cdot \frac{P}{r^3}, \quad (10)$$

where $\alpha_{\text{dyn.}}$ is the real part of the optical complex polarizability of the molecule in the region of the corresponding absorption band, n_D is the index of refraction of the solvent for the frequencies of the light field, and $E_{\text{eff.}}$ is the effective internal field of the light wave acting on the molecule in the solvent.

When we substitute (8)-(10) into expressions (2)-(6), integrate, and for simplicity assume $\alpha/r^3 \approx 1/2$ (see refs. 20 and 21), we obtain

$$hc\Delta\nu'_{\text{or.}} = \frac{2\mu_g}{r^3} \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right] (\mu_g^p - \mu_s^{\text{eff.}}), \quad (11)$$

$$hc\Delta\nu'_{\text{or.}} = \frac{2\mu_s}{r^3} \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right] (\mu_g^{\text{eff.}} - \mu_s^p), \quad (12)$$

$$hc\Delta\nu'_{\text{ind.}} = \frac{1}{r^3} \left(\frac{n_0^2 - 1}{n_0^2 + 2} \right) (\mu_g^p - \mu_s^{\text{eff.}}), \quad (13)$$

$$hc\Delta\nu'_{\text{ind.}} = \frac{1}{r^3} \left(\frac{n_0^2 - 1}{n_0^2 + 2} \right) (\mu_g^{\text{eff.}} - \mu_s^p), \quad (14)$$

$$hc\Delta\nu''_{\text{dyn.}} = -\frac{P_0^2}{r^3} \frac{n_D^2 - 1}{2n_D^2 + 1}. \quad (15)$$

It is easy to see that the problem reduces finally to the determination of the dipole moments of the solute molecule in the corresponding electronic states.

Let us now calculate these parameters. According to the Onsager theory, the values of the permanent dipole moments of the solute molecule in the ground (μ_g^p) and excited (μ_s^p) equilibrium states will be written in the form

$$\mu_g^p = \mu_g + \alpha R_g, \quad \mu_s^p = \mu_s + \alpha R_s, \quad (16)$$

from which for $\alpha/r^3 \approx 1/r$ we obtain

$$\mu_g^p = \mu_g \frac{2\varepsilon + 1}{\varepsilon + 2}, \quad \mu_s^p = \mu_s \frac{2\varepsilon + 1}{\varepsilon + 2}. \quad (17)$$

The calculation of the moments corresponding to nonequilibrium states is a little more complex. The expressions for the projections of moments μ_g^{H} and μ_s^{H} in the directions of the fields $R_{g(\text{or.})}$ and $R_{s(\text{or.})}$ (Fig. 2,b,c) are written as follows

$$\mu_{g\parallel}^{\text{H}} = \mu_g + \alpha [R_{g(\text{or.})} \cos \alpha + R_{s(\text{ind.})}^{\text{H}} \cos (\alpha - \beta)], \quad (18)$$

$$\mu_{s\parallel}^{\text{H}} = \mu_s + \alpha [R_{s(\text{or.})} \cos \alpha + R_{g(\text{ind.})}^{\text{H}} \cos (\alpha - \gamma)]. \quad (19)$$

The values of the projections perpendicular to the above-mentioned directions are given by

$$\mu_{g\perp}^{\text{H}} = \alpha [R_{g(\text{or.})} \sin \alpha + R_{s(\text{ind.})}^{\text{H}} \sin (\alpha - \beta)], \quad (20)$$

$$\mu_{s\perp}^{\text{H}} = \alpha [R_{s(\text{or.})} \sin \alpha + R_{g(\text{ind.})}^{\text{H}} \sin (\alpha - \gamma)]. \quad (21)$$

It is not difficult to see that

$$\mu_{\text{eff.}}^{\text{H}} = \mu_{\text{eff.}}^{\text{H}} + \mu_{\text{eff.}}^{\text{H}}; \quad \mu_{\text{eff.}}^{\text{H}}(\text{eff.}) = \mu_{\text{eff.}}^{\text{H}} \cos \alpha + \mu_{\text{eff.}}^{\text{H}} \sin \alpha. \quad (22)$$

Substitution (16)-(22) into (11)-(15), and performing some simple but cumbersome calculations, we obtain

$$hc\Delta\nu'_{\text{or.}} = \frac{2\mu_g}{r^3} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right) \left[(\mu_g - \mu_s \cos \alpha) \frac{2n_0^2 + 1}{n_0^2 + 2} - \mu_g \frac{n_0^2 - 1}{n_0^2 + 2} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right) \right]; \quad (23)$$

$$hc\Delta\nu'_{\text{or.}} = \frac{2\mu_s}{r^3} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right) \left[(\mu_g \cos \alpha - \mu_s) \frac{2n_0^2 + 1}{n_0^2 + 2} + \mu_s \frac{n_0^2 - 1}{n_0^2 + 2} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right) \right]; \quad (24)$$

$$hc\Delta\nu'_{\text{ind.}} = \frac{1}{r^3} \frac{n_0^2 - 1}{n_0^2 + 2} \left\{ \mu_g^2 \left[\left(\frac{2\varepsilon + 1}{\varepsilon + 2} \right)^2 - \left(\frac{2n_0^2 + 1}{n_0^2 + 2} \right)^2 \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right)^2 \right] - \left(\frac{2n_0^2 + 1}{n_0^2 + 2} \right)^2 \left[\mu_s^2 + 2\mu_g \mu_s \cos \alpha \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right) \right] \right\}; \quad (25)$$

$$hc\Delta\nu'_{\text{ind.}} = \frac{1}{r^3} \frac{n_0^2 - 1}{n_0^2 + 2} \left\{ \left(\frac{2n_0^2 + 1}{n_0^2 + 2} \right)^2 \left[\mu_g^2 + 2\mu_g \mu_s \cos \alpha \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right) \right] - \mu_s^2 \left[\left(\frac{2\varepsilon + 1}{\varepsilon + 2} \right)^2 - \left(\frac{2n_0^2 + 1}{n_0^2 + 2} \right)^2 \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right)^2 \right] \right\}. \quad (26)$$

From this we obtain the following expression for the orientation-induction shift of the frequency

$$\nu^{\text{e}} \left(\Delta\nu^{\text{e}} = \frac{\Delta\nu^{\text{e}} + \Delta\nu^{\text{f}}}{2} \right)$$

(ref. 5):

$$hc\Delta\nu^{\text{e}} = \frac{(\mu_g^2 - \mu_s^2)}{r^3} \left[\frac{\varepsilon - 1}{\varepsilon + 2} \left(\frac{2n_0^2 + 1}{n_0^2 + 2} \right)^2 - \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right)^2 \left(\frac{2n_0^2 + 1}{n_0^2 + 2} \right) \frac{n_0^2 - 1}{n_0^2 + 2} \right]. \quad (27)$$

After a number of transformations, we obtain the following simplified expressions for the values of orientation-induction shifts of frequencies ν^{a} , ν^{f} , and ν^{e} :

$$hc\Delta\nu^{\text{a}} = \frac{(2n_0^2 + 1)^2}{r^3 (n_0^2 + 2)^2} \left[2\mu_g (\mu_g - \mu_s \cos \alpha) \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right) + (\mu_g^2 - \mu_s^2) \frac{n_0^2 - 1}{n_0^2 + 2} \right]; \quad (28)$$

$$hc\Delta\nu^{\text{f}} = \frac{(2n_0^2 + 1)^2}{r^3 (n_0^2 + 2)^2} \times \left[2\mu_s (\mu_g \cos \alpha - \mu_s) \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right) + (\mu_g^2 - \mu_s^2) \frac{n_0^2 - 1}{n_0^2 + 2} \right]; \quad (29)$$

$$hc\Delta\nu^{\text{e}} = \frac{(2n_0^2 + 1)^2}{r^3 (n_0^2 + 2)^2} (\mu_g^2 - \mu_s^2) \frac{\varepsilon - 1}{\varepsilon + 2}. \quad (30)$$

Furthermore, the moment P_0 [formula (15)], which is considered as the dipole moment of the transition from the e state, is proportional to the oscillator strength²² f ,

$$|P_0|^2 = \frac{he^2 f}{8\pi^2 m \nu_0}, \quad (31)$$

where ν_0 is the frequency of the electronic transition of the investigated molecule in the vapor state. We therefore obtain the following expression for the magnitude of the dynamic shift:

$$hc\Delta\nu_{\text{dyn}}^{\nu^a, f, s} = -\frac{he^2 f}{8\pi^2 m \nu_0^3} \cdot \frac{n_D^2 - 1}{2n_D^2 + 1}. \quad (32)$$

It is readily seen that expression (32) coincides with Rayleigh's formula,²³ which was obtained by a different method.

Finally, we obtain the following approximate expressions for the total shift of the frequencies of the electronic transitions ν^a and ν^f , and also ν^s :

$$hc\Delta\nu^a(f) = \frac{(2n_0^2 + 1)^2}{(n_0^2 + 2)^2} \left[C_1(f) \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right) + C_2 \frac{n_0^2 - 1}{n_0^2 + 2} \right] + C_3 \frac{n_0^2 - 1}{2n_D^2 + 1}, \quad (33)$$

$$hc\Delta\nu^s = \frac{(2n_0^2 + 1)^2}{(n_0^2 + 2)^2} C_2 \left(\frac{\epsilon - 1}{\epsilon + 2} \right) + C_3 \frac{n_0^2 - 1}{2n_D^2 + 1}, \quad (34)$$

where the constants C_1 , C_2 , and C_3 are determined by the properties of the solute molecule, and are calculated from formulas (28)–(30). It should be noted that negative values of these constants correspond to a red shift and positive values correspond to a blue shift.

Analysis of expressions (23)–(34) shows that they are substantially different from those obtained in refs. 1–7. First of all, the magnitude of the spectral shift in the general case depends not only on the ratio of the dipole moments μ_g and μ_e but also on the angle α between the directions of these moments. The nature of this dependence is different for absorption and emission spectra. It is characteristic that the position of the frequency ν^s does not depend on the angle α but is determined entirely by the change in the dipole moment during the absorption or emission of light.

The nature of the dependence of the position of spectra on the index of refraction n_0 , which is extrapolated to infinite wavelength, is essentially different from that given in refs. 1–7. It is easy to see that this dependence shows up more clearly, since the term including n_0 enters into the general expressions for the spectral shifts in particular in the form of a multiplier.

A detailed review of the relationships obtained will be given later, when the corresponding experimental data are discussed. We will only remark now that expressions (23)–(24) in general describe all possible combinations: from the case of dipolar molecules in polar solvents to nonpolar molecules in nonpolar media.

These expressions show very distinctly the universal character of the internal field effect on the spectral characteristics of the solute molecules. Of course, a dependence on the index of refraction of the solvent must exist in all cases, since the very existence of the spectra ($f \neq 0$) requires them to shift. A dependence on the dielectric constant of the medium, determined by the nature of the change of the permanent dipole moments of the molecule during excitation and by their relative

orientation, can also occur in a very large number of cases (polar molecules). Thus, the over-all effect of the internal field which is determined by the relations between orientation, induction, and dynamic effects, depends ultimately on geometric, electrical, and optical microscopic parameters of the solute molecule, and on generalized physical properties of the solvent.

In conclusion, we wish to note that the investigation of the internal field's influence represents a generalized method for calculating the intermolecular interactions of a dipole nature, i.e., orientation and induction effects. Along with this, still another type of van der Waals interactions exists. It also has a universal character, although it is not considered in the theory presented above. The problem concerns dispersive interactions, whose energy in many cases may be considerable. Let us investigate this problem in more detail.

It is known that the energy of interaction, as determined by dispersive powers, can be expressed as a function of the polarizabilities of the interacting molecules, i.e.,²⁴

$$W_{\text{disp.}} = -\frac{3}{2} \frac{I I'}{I + I'} \alpha \alpha' \sum_{i=1}^{\infty} \frac{1}{R_i^6}, \quad (35)$$

where I , I' and α , α' are the ionization potentials and polarizabilities of the solute molecule and the surrounding solvent molecules respectively (k is the number of closest neighbors), and R is the distance between molecules. Considering that

$$\alpha' = r^3 \frac{n^2 - 1}{n^2 + 2}, \quad (36)$$

where n is the index of refraction, and r is the radius of the solvent molecule, it is not difficult to obtain the following approximate expression for the magnitude of the spectral shift caused by dispersive interactions:

$$hc\Delta\nu_{\text{disp.}} = C_4' (\alpha_g - \alpha_e) \frac{n_D^2 - 1}{n_D^2 + 2} = C_4' \frac{n_D^2 - 1}{n_D^2 + 2}, \quad (37)$$

(α_g and α_e are the polarizabilities of the investigated molecule in the ground and excited states respectively, and C_4' is a parameter which depends on a number of properties of the solute and solvent molecules).

It is easy to see that, with respect to the nature of the dependence on the solvent's index of refraction, this expression does not differ from the expressions obtained above. At different α_e/α_g ratios, the interactions in question can produce essentially minor shifts to the blue or, more frequently, to the red (usually $\alpha_e > \alpha_g$). Therefore, expression (37) must be present in the general relationships (6), (33), and (34), which determine the magnitude of the spectral shift of the molecules investigated resulting from the transition from the vapor to the solution state.

On the basis of the preceding discussion, the final expressions derived for the shift of frequencies ν^a , ν^f , and ν^s , using the Onsager-Böttcher model, can be written in the form

$$hc\Delta\nu^a(f) = \frac{(2n_0^2 + 1)^2}{(n_0^2 + 2)^2} \left[C_1(f) \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right) + C_2 \frac{n_0^2 - 1}{n_0^2 + 2} \right] + C_3 \frac{n_D^2 - 1}{2n_D^2 + 1} + C_4' \frac{n_D^2 - 1}{n_D^2 + 2}, \quad (38)$$

$$hc\Delta\nu^s = C_2 \left[\frac{\epsilon - 1}{\epsilon + 2} \left(\frac{2n_0^2 + 1}{n_0^2 + 2} \right)^3 - \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n_0^2 - 1}{n_0^2 + 2} \right) \left(\frac{2n_0^2 + 1}{n_0^2 + 2} \right) \frac{n_0^2 - 1}{n_0^2 + 2} \right] + C_3 \frac{n_D^2 - 1}{2n_D^2 + 1} + C_4' \frac{n_D^2 - 1}{n_D^2 + 2}. \quad (39)$$

REFERENCES

1. Y. Ooshika, J. Phys. Soc. Japan 9, 594 (1954).
2. N. Mataga, Y. Kaifu, and M. Koizumi, Bull. Chem. Soc. Japan 28, 690 (1955); Ibid. 29, 465 (1956).
3. E. McRae, J. Phys. Chem. 61, 562 (1957).
4. L. Onsager, J. Am. Chem. Soc. 58, 1485 (1936).
5. N. G. Bakhshiev, Izvest. Akad. Nauk SSSR, Ser. Fiz. 22, 1387 (1958); Opt. i Spekt. 7, 52 (1959), Optics and Spectroscopy 7, 29 (1959).
6. N. G. Bakhshiev, Candidate's dissertation, Gosudarst. Opt. Inst., Leningrad, 1959.
7. O. Popovich and L. Rogers, J. Am. Chem. Soc. 81, 4469 (1959).
8. B. S. Neporent and N. G. Bakhshiev, Opt. i Spekt. 8, 777 (1960), Optics and Spectroscopy 8, 408 (1960).
9. N. Baylis and E. McRae, J. Phys. Chem. 58, 1002 (1954).
10. B. S. Neporent, Zhur. Fiz. Khim. 30, 1048 (1956); Trudy Gosudarst. Opt. Inst. 25, issue 150, 3 (1957).
11. E. Lippert, Z. Elektrochem. 61, 962 (1957).
12. D. Whiffen, Quart. Rev. Chem. Soc. 4, 131 (1950).
13. J. Kirkwood, J. Chem. Phys. 7, 911 (1939); Ibid. 8, 205 (1940).
14. U. Frölich, Trans. Faraday Soc. 44, 238 (1948); "Theory of Dielectrics," London, 1949.
15. F. Harris and B. Alder, J. Chem. Phys. 21, 1031 (1953); Ibid. 22, 1806 (1954).
16. A. Buckingham, Proc. Roy. Soc. (London) A238, 235 (1956).
17. A. Dekker, Physica 12, 209 (1946); D. Frood and A. Dekker, J. Chem. Phys. 20, 1030 (1952); T. Scholte, J. Chem. Phys. 21, 2087 (1953).
18. Ya. I. Frenkel' and A. I. Gubanov, Uspekhi Fiz. Nauk 24, 68 (1940).
19. L. G. Pikulik, Izvest. Akad. Nauk SSSR, Ser. Fiz. 24, 572 (1960).
20. N. G. Bakhshiev, Opt. i Spekt. 5, 646 (1958).
21. C. Böttcher, "Theory of Electric Polarization," Elsevier, Amsterdam and Van Nostrand, New York, 1952.
22. B. I. Stepanov, "Luminescence of Complex Molecules," Izd. Akad. Nauk Belorus.SSR, Minsk, 1955.
23. N. Bayliss, J. Chem. Phys. 18, 292 (1950).
24. S. Veljkovic, Trans. Faraday Soc. 53, 1181 (1957).

CHARACTERISTICS OF LIGHT ABSORPTION AND LUMINESCENCE IN LOW-CONCENTRATION SOLID BINARY SOLUTIONS

A. F. Lubchenko (pp. 727-736)

Received 4 July 1960

A theory of light absorption and luminescence is developed for solid solutions in which impurity molecules of the same or different chemical compounds are distributed in pairs. The distance between pairs is assumed to be much greater than the distance between the molecules forming the pair, so that the interaction energy of pairs is negligible compared to the interaction energy of a pair of impurity molecules.

INTRODUCTION

The theory of the optical properties of dilute solutions has been developed in many papers.¹⁻⁷ With the aid of fairly general assumptions, formulas have been obtained for the shape of absorption, luminescence, and dispersion curves in the region of impurity absorption. Analytical expressions have also been derived for the probability of radiationless transition^{7,8} and the mean radiation lifetime of an impurity center in the excited state.^{5,9}

Recent years have witnessed experimental studies of the optical properties of solutions at concentrations such that the interaction between impurity centers can no longer be disregarded; that is, there is a possibility that impurity molecules form groups of several molecules. In addition to this, according to the hypothesis of Kitai-gorodskii,^{10,11} when molecules which do not have centers of symmetry form even dilute solutions, these molecules are distributed in the crystal by pairs in such a way that each such pair has a center of symmetry if the site-group of molecules of the crystal has a center of inversion. This situation creates the need for a theoretical study of the optical properties of such solutions.

In this paper it is assumed that the impurity molecules (of the same or different chemical compounds) form

pairs, and that the interaction between pairs is negligible compared to the interaction between the molecules of a pair. All of the calculations are carried out without any detailed assumptions as to the nature of the impurity molecules (atoms) or the solvent.

THE WAVE FUNCTIONS OF A BINARY SOLUTION

The Hamiltonian of a solution containing a pair of interacting impurity centers has the form

$$H = \sum_i \hbar \omega_i \left(-\frac{\partial^2}{\partial \xi_i^2} + \xi_i^2 \right) + H_1 + H_2 + V_1 + V_2 + V_{12} \quad (1)$$

H_1 and H_2 are the Hamiltonian operators of the first and second impurity centers, respectively, V_{12} is the operator of the energy of interaction between them, V_1 and V_2 are operators of the energy of interaction of the first and second impurity centers with the solvent, ξ_i and ω_i are respectively the normal coordinates and normal vibrational frequency of the solution (the index s designates the values of the wave vector of vibration and number of the branch in question, considered together).

As is well known, the eigenvalues of operator (1) are the extreme values of the functional

$$H[\Psi(\mathbf{r}_1\mathbf{r}_2q_1q_2\xi_s)] = \int \Psi^*(\mathbf{r}_1\mathbf{r}_2q_1q_2\xi_s) H\Psi(\mathbf{r}_1\mathbf{r}_2q_1q_2\xi_s) d\tau \quad (2)$$

under the additional conditions

$$\int \Psi^*(\mathbf{r}_1\mathbf{r}_2q_1q_2\xi_s) \Psi(\mathbf{r}_1\mathbf{r}_2q_1q_2\xi_s) d\tau = \delta_{\gamma\gamma'}, \quad (3)$$

where

$$d\tau = d\mathbf{r}_1 d\mathbf{r}_2 dq_1 dq_2 d\xi_s, \quad d\xi_s = \prod_i d\xi_{s_i}, \quad \mathbf{r}_1 q_1 \text{ and } \mathbf{r}_2 q_2$$

are, respectively, the coordinates of the electrons and the normal coordinates of the internal vibrations of the first and second impurity centers; γ and γ' correspond to full sets of quantum numbers which characterize the state of the solution. The functions $\Psi(\mathbf{r}_1\mathbf{r}_2q_1q_2\xi_s)$ extremizing functional (2) are eigenfunctions of the operator H . We will look for wave functions of the ground state of the solution in the form

$$\Psi_{0(n_s)} = [(S_1 + S_2)!]^{-1/2} \sum_s (-)^s P_{s,\gamma_1}(\mathbf{r}_1 q_1) \varphi_2^0(\mathbf{r}_2 q_2) F_{n_s}(\xi_s), \quad (4)$$

where S_1 and S_2 are respectively the number of electrons in the first and second impurity centers, and P_{ν} is the operator for transposition of electrons between the impurity centers.

Assuming that the amplitudes of vibration of the nuclei of the solution are small, and expanding V_1 , V_2 , V_{12} as a series in powers of ξ_s ,

$$\left. \begin{aligned} V_1 &= V_{10}(\mathbf{r}_1 q_1) + \sum_s V_{1s} \xi_s + \dots \\ V_2 &= V_{20}(\mathbf{r}_2 q_2) + \sum_s V_{2s} \xi_s + \dots \\ V_{12} &= V_{120}(\mathbf{r}_1 q_1 \mathbf{r}_2 q_2) + \sum_s V_{12s} \xi_s + \dots \end{aligned} \right\} \quad (5)$$

we obtain, after substituting (4) and (5) into (2),

$$H[\varphi_1^0 \varphi_2^0] = \frac{1}{2} \int F_{n_s}^*(\xi_s) \sum_s \hbar \omega_s \times \left[-\frac{\partial^2}{\partial \xi_s^2} + (\xi_s - \xi_{s0})^2 \right] F_{n_s}(\xi_s) d\xi_s + J[\varphi_1^0 \varphi_2^0]. \quad (6)$$

where

$$\begin{aligned} J[\varphi_1^0 \varphi_2^0] &= V_{10}[\varphi_1^0] + V_{20}[\varphi_2^0] \\ &+ V_{120}[\varphi_1^0 \varphi_2^0] + H_1[\varphi_1^0] + H_2[\varphi_2^0] - \frac{1}{2} \sum_s \hbar \omega_s \xi_{s0}^2, \\ \xi_{s0} &= -\frac{(V_{1s}[\varphi_1^0] + V_{2s}[\varphi_2^0] + V_{12s}[\varphi_1^0 \varphi_2^0])}{\hbar \omega_s}, \end{aligned}$$

$$V_{12s}[\varphi_1^0 \varphi_2^0] = \int \varphi_1^{*0} \varphi_2^{*0} V_{12s} \varphi_1^0 \varphi_2^0 d\mathbf{r}_1 d\mathbf{r}_2 dq_1 dq_2 + \text{exchange terms},$$

$$J_{\lambda\sigma}[\varphi_j^0] = \int \varphi_j^0 \chi_{j\sigma} \varphi_j^0 d\mathbf{r}_j dq_j; \quad \chi_{j\sigma} = V_{1\sigma}, \quad V_{2\sigma}, \quad H_1, \quad H_2; \quad \sigma = 0, s.$$

The functional (6) must be minimized by independently varying φ_1^0 , φ_2^0 and $F_{n_s}(\xi_s)$ with the additional condition (3). Variation of (6) with respect to F_{n_s} , with φ_1^0 and φ_2^0 fixed, leads to the following Euler equation:

$$\frac{1}{2} \sum_s \hbar \omega_s \left[-\frac{\partial^2}{\partial \xi_s^2} + (\xi_s - \xi_{s0})^2 \right] F_{n_s}(\xi_s) = \Delta F_{n_s}(\xi_s).$$

The solution of this equation, as is well known, has the form

$$\Delta = \sum_s \hbar \omega_s \left(n_s + \frac{1}{2} \right), \quad F_{n_s}(\xi_s) = \prod_i f_{n_s}(\xi_s - \xi_{s0}), \quad (7)$$

where

$$f_{n_s}(\xi_s - \xi_{s0}) = C_{n_s} e^{-1/2(\xi_s - \xi_{s0})^2} H_{n_s}(\xi_s - \xi_{s0}), \quad H_{n_s}$$

are Tchebycheff-Hermitean polynomials and C_{n_s} is a normalization constant.

After substituting (7) into (6), we obtain the functional

$$H[\varphi_1^0 \varphi_2^0] = J[\varphi_1^0 \varphi_2^0] + \sum_s \hbar \omega_s \left(n_s + \frac{1}{2} \right),$$

which must be further minimized by varying φ_1^0 and φ_2^0 under the added condition (3). The variation leads to the following Euler equations:

$$\left. \begin{aligned} H_1 \varphi_1^0 + V_{10} \varphi_1^0 + V_{120} [\varphi_2^0] \varphi_1^0 + \sum_s \xi_{s0} \{ V_{1s} \varphi_1^0 + V_{12s} [\varphi_2^0] \varphi_1^0 \} &= \epsilon_1^0 \varphi_1^0, \\ H_2 \varphi_2^0 + V_{20} \varphi_2^0 + V_{120} [\varphi_1^0] \varphi_2^0 + \sum_s \xi_{s0} \{ V_{2s} \varphi_2^0 + V_{12s} [\varphi_1^0] \varphi_2^0 \} &= \epsilon_2^0 \varphi_2^0. \end{aligned} \right\} \quad (8)$$

Let us assume that we have found the solutions of (8) and determined ϵ_1^0 and ϵ_2^0 and the corresponding energy values ϵ_1^0 and ϵ_2^0 . Note that even if the operators H_1 and H_2 are identical, i.e., even if the impurity centers are the same outside the solvent, in the solution their wave functions and the energy levels corresponding to them can turn out to be different, due to differences in V_1 and V_2 . Starting from (8), it is easily shown that

$$J[\varphi_1^0 \varphi_2^0] = \epsilon_1^0 + \epsilon_2^0 + \frac{1}{2} \sum_s \hbar \omega_s \xi_{s0}^2 - \sum_s \xi_{s0} V_{12s} [\varphi_1^0 \varphi_2^0] - V_{120} [\varphi_1^0 \varphi_2^0],$$

The wave functions of the solution in the ground state and the corresponding energy eigenvalues can be written in the form

$$\left. \begin{aligned} \Psi_{0(n_s)} &= [(S_1 + S_2)!]^{-1/2} \sum_s (-)^s P_{s,\gamma_1}(\mathbf{r}_1 q_1) \varphi_2^0(\mathbf{r}_2 q_2) \prod_i f_{n_s}(\xi_s - \xi_{s0}), \\ E_{0(n_s)} &= J[\varphi_1^0 \varphi_2^0] + \sum_s \hbar \omega_s \left(n_s + \frac{1}{2} \right). \end{aligned} \right\} \quad (9)$$

Assuming that the absorption band of the impurity is located far from the solvent absorption band, we will look for wave functions of the excited state in the form*

*We assume in addition that the spacing between split electron levels of the pair of impurity molecules is greater than the vibrational energy $\hbar \omega_s$ ($s = 1, 2, \dots$).

$$\Psi_{\lambda(n_s)} = \frac{1}{\sqrt{2}} (a_1 \Phi_{10} + a_2 \Phi_{0\lambda}) F_{n_s}(\xi_s), \quad (10)$$

where

$$\Phi_{10} = [(S_1 + S_2)!]^{-1/2} \sum_s (-)^s P_{s,\gamma_1} \varphi_1^0 \varphi_2^0,$$

$$\Phi_{0\lambda} = [(S_1 + S_2)!]^{-1/2} \sum_s (-)^s P_{s,\gamma_1} \varphi_1^0 \varphi_2^\lambda,$$

with $(\Phi_{10}^* \Phi_{0\lambda}) = 0$. Then after substituting (1), (5), and (10) into (2) and integrating over all variable systems, we obtain the functional

$$\begin{aligned} H[\varphi_1^0 \varphi_2^\lambda] &= \frac{1}{2} \int F_{n_s}^*(\xi_s) \sum_s \hbar \omega_s \left[-\frac{\partial^2}{\partial \xi_s^2} + (\xi_s - \xi_{s0})^2 \right] \\ &\times F_{n_s}(\xi_s) d\xi_s + J[\varphi_1^0 \varphi_2^\lambda]. \end{aligned} \quad (11)$$

where

$$\begin{aligned}
J[\varphi_1^i \varphi_2^i a_1 a_2] &= \frac{|a_1|^2}{2} \{a_1 + H_1[\varphi_1^i] + V_{10}[\varphi_1^i] + V_{120}[\varphi_1^i \varphi_2^0]\} \\
&+ \frac{|a_2|^2}{2} \{a_2 + H_2[\varphi_2^i] + V_{20}[\varphi_2^i] + V_{120}[\varphi_1^0 \varphi_2^i]\} + \frac{a_1^* a_2^*}{2} V_{120}[\varphi_1^0 \varphi_2^i \varphi_2^0] \\
&+ \frac{a_1^* a_2^*}{2} V_{120}[\varphi_1^i \varphi_2^0 \varphi_2^i], \\
a_1 &= H_1[\varphi_1^0] + V_{10}[\varphi_1^0], \quad a_2 = H_2[\varphi_2^0] + V_{20}[\varphi_2^0], \\
V_{120}[\varphi_1^0 \varphi_2^i \varphi_2^0] &= \int \varphi_1^0 \varphi_2^i V_{120}^* \varphi_2^0 d\tau_1 d\tau_2 + \text{exchange terms}, \\
V_{120}[\varphi_1^i \varphi_2^0] &= \int \varphi_1^i \varphi_2^0 V_{120}^* \varphi_2^0 d\tau_1 d\tau_2 + \text{exchange terms}, \\
\varepsilon_{s1\lambda} &= -\frac{f_{1s} + f_{2s} + f_{3s}}{\hbar\omega_s}; \\
f_{1s} &= |a_1|^2 V_{1s}[\varphi_1^i] + |a_2|^2 V_{1s}[\varphi_1^0], \\
f_{2s} &= |a_1|^2 V_{2s}[\varphi_2^i] + |a_2|^2 V_{2s}[\varphi_2^0], \\
f_{3s} &= |a_1|^2 V_{12s}[\varphi_1^i \varphi_2^0] + a_1^* a_2 V_{12s}[\varphi_1^i \varphi_2^0 \varphi_2^i] \\
&+ |a_2|^2 V_{12s}[\varphi_1^0 \varphi_2^i] + a_2^* a_1 V_{12s}[\varphi_1^0 \varphi_2^i \varphi_2^0]. \quad (12)
\end{aligned}$$

Varying (11) with respect to $F_{n_s}^*(\xi_s)$ we obtain the Euler equation

$$\begin{aligned}
\frac{1}{2} \sum_s \hbar\omega_s \left[-\frac{\partial^2}{\partial \xi_s^2} + (\xi_s - \varepsilon_{s1\lambda})^2 \right] F_{n_s}(\xi_s) \\
= \left(\Lambda + \frac{1}{2} \sum_s \hbar\omega_s \varepsilon_{s1\lambda}^2 \right) F_{n_s}(\xi_s),
\end{aligned}$$

the solutions of which have the form

$$\left. \begin{aligned}
\Lambda &= \sum_s \hbar\omega_s \left(n_s + \frac{1}{2} \right) - \frac{1}{2} \sum_s \hbar\omega_s \varepsilon_{s1\lambda}^2, \\
F_{n_s}(\xi_s) &= \prod_s f_{n_s}(\xi_s - \varepsilon_{s1\lambda}).
\end{aligned} \right\} \quad (13)$$

Thus the functional (11) can be rewritten in the form

$$H[\varphi_1^i \varphi_2^i] = J[\varphi_1^i \varphi_2^i a_1 a_2] + \sum_s \hbar\omega_s \left(n_s + \frac{1}{2} \right) - \frac{1}{2} \sum_s \hbar\omega_s \varepsilon_{s1\lambda}^2. \quad (14)$$

This functional must be minimized by varying φ_1^i , φ_2^i , a_1 , and a_2 independently.

The extremely complex system of integral-differential equations thus obtained cannot be solved exactly, so we used the method of successive approximation. In connection with this we note that φ_1^0 and φ_2^0 , which enter the expression for the matrix elements (12), are known exactly as solutions of the equations (8), so that numerical values are available for α_1 and α_2 . The sum of the terms in (12), which includes $a_1^* a_2$ and $a_1 a_2^*$ as multipliers, together with the sum $\sum_s \varepsilon_{s1\lambda}^2 \hbar\omega_s$ is much smaller than the sum $\{|a_2|^2 V_{20}[\varphi_2^i] + |a_1|^2 V_{10}[\varphi_1^i]\}$ for any possible values of a_1 and a_2 . On this basis they can be neglected in those Euler equations which are derived from (14) by varying φ_1^i and φ_2^i . Then the latter are written in the form

$$\left. \begin{aligned}
H_1 \varphi_1^i + V_{10} \varphi_1^i + V_{12}[\varphi_2^0] \varphi_1^i &= \varepsilon \varphi_1^i, \\
H_2 \varphi_2^i + V_{20} \varphi_2^i + V_{12}[\varphi_1^0] \varphi_2^i &= \varepsilon \varphi_2^i.
\end{aligned} \right\} \quad (15)$$

Let us assume that we have found the solutions to (15), i.e., φ_1^i and φ_2^i and the corresponding eigenvalues of the energy ε_1^i and ε_2^i . As is seen from (15) these solutions differ from solutions for free impurity centers, since the zero term of the expansion of the energy of

interaction of the impurity centers with the solvent enters into (15). Because of this, free impurity centers which are identical in nature can turn out to be different in solution as a consequence of a difference in their "deformation" by the solvent (when they are embedded in different sites in the unit cell or replace solvent molecules located at nonequivalent lattice points).

We substitute the solutions of (15) that were found into the expressions for $V_{120}[\varphi_1^0 \varphi_2^i \varphi_2^0]$ ($\sigma = 0, s$). Then the functional (12) is written in the form

$$\begin{aligned}
J[a_1 a_2] &= \frac{|a_1|^2}{2} A_1 + \frac{|a_2|^2}{2} A_2 + \frac{1}{2} a_1^* a_2 V_{120}[\varphi_1^0 \varphi_2^i \varphi_2^0] \\
&- \frac{1}{2} \sum_s \hbar\omega_s \varepsilon_{s1\lambda}^2 + \frac{1}{2} a_1^* a_2 V_{120}[\varphi_1^i \varphi_2^0 \varphi_2^i],
\end{aligned}$$

where $A_1 = a_1 + \varepsilon_1^i$, $A_2 = a_2 + \varepsilon_2^i$; moreover, in view of the functions φ_1^i , φ_2^i , φ_1^0 , φ_2^0 being real,

$$V_{120}[\varphi_1^0 \varphi_2^i \varphi_2^0] = V_{120}[\varphi_1^i \varphi_2^0 \varphi_2^i] \equiv V_{120}, \quad (\sigma = 0, s).$$

Varying the functional further with respect to a_1^* and a_2^* we obtain the system of equations

$$\left. \begin{aligned}
a_1 \left(\partial - A_1 - \sum_s \varepsilon_{s1\lambda} B_{1s} \right) &= a_2 V_{120} + a_2 \sum_s \varepsilon_{s1\lambda} V_{12s}, \\
a_2 \left(\partial - A_2 - \sum_s \varepsilon_{s1\lambda} B_{2s} \right) &= a_1 V_{120} + a_1 \sum_s \varepsilon_{s1\lambda} V_{12s},
\end{aligned} \right\} \quad (16)$$

where

$$\begin{aligned}
B_{1s} &= V_{1s}[\varphi_1^i] + V_{2s}[\varphi_2^0] + V_{12s}[\varphi_1^i \varphi_2^0], \\
B_{2s} &= V_{1s}[\varphi_1^0] + V_{2s}[\varphi_2^i] + V_{12s}[\varphi_1^0 \varphi_2^i],
\end{aligned}$$

in which the values $\varepsilon_{s1\lambda}$ are functions of a_1 and a_2 . We will solve this system using the perturbation method, assuming that A and V_{120} are values of the zeroth order of smallness and that all components containing $\varepsilon_{s1\lambda}$ are of the first order of smallness (proportional to a small quantity δ). Then, assuming

$$a_1 = a_{10} + \delta a_{11}, \quad a_2 = a_{20} + \delta a_{21}, \quad \partial = \partial_0 + \delta \partial',$$

we obtain in the place of systems (16) that two systems of equations

$$\left. \begin{aligned}
a_{10}(\partial_0 - A_1) &= a_{20} V_{120}, \\
a_{20}(\partial_0 - A_2) &= a_{10} V_{120}
\end{aligned} \right\} \quad (17)$$

with the condition that

$$a_{10}^2 + a_{20}^2 = 2,$$

and

$$\left. \begin{aligned}
a_{10} \partial' + a_{11}(\partial_0 - A_1) &= a_{21} V_{120} + \beta_1, \\
a_{20} \partial' + a_{21}(\partial_0 - A_2) &= a_{11} V_{120} + \beta_2
\end{aligned} \right\} \quad (18)$$

under the condition that $a_{10} a_{21} + a_{20} a_{11} = 0$. Here

$$\begin{aligned}
\beta_1 &= a_{10} \sum_s \varepsilon_{s1\lambda} (a_{10} a_{20}) B_{1s} + a_{20} \sum_s \varepsilon_{s1\lambda} (a_{10} a_{20}) V_{12s}, \\
\beta_2 &= a_{20} \sum_s \varepsilon_{s1\lambda} (a_{10} a_{20}) B_{2s} + a_{10} \sum_s \varepsilon_{s1\lambda} (a_{10} a_{20}) V_{12s}.
\end{aligned}$$

The system of equations (17) together with the added conditions make it possible to determine the values of a_{10} , a_{20} , and ∂_0 . Thus

$$\partial_0^{\pm} = \frac{(A_1 + A_2) \pm \sqrt{(A_1 - A_2)^2 + 4V_{120}^2}}{2}, \quad a_{10}^+, a_{20}^+, a_{10}^-, a_{20}^-. \quad (19)$$

We find the correction in the first approximation from (18)

$$\begin{aligned}\vartheta' &= \frac{1}{2} (a_{10}\beta_1 + a_{20}\beta_2), \\ a_{11} &= -\frac{a_{10}\beta_2 - a_{20}\beta_1}{4V_{120}} a_{10}a_{20}, \\ a_{21} &= \frac{a_{10}\beta_2 - a_{20}\beta_1}{4V_{120}} a_{20}a_{10}.\end{aligned}\quad (20)$$

We will consider the solution of (17) for three cases

$$\left. \begin{aligned}1) A_I &= A_\lambda, \\ 2) (A_I - A_\lambda)^2 &\ll 4V_{120}^2, \\ 3) (A_I - A_\lambda)^2 &\gg 4V_{120}^2.\end{aligned} \right\} \quad (21)$$

The first case occurs when the impurity molecules are the same and are identically disposed in the solvent, so that their interactions with the solvent are also identical. In particular, this situation will be realized if the hypothesis of A. I. Kitaigorodskii is true for impurity molecules without a center of inversion when the unit cell of the solvent has a center of inversion. In this case, (19) and (20) give us

$$\begin{aligned}\vartheta_0^\pm &= A_I \pm |V_{120}|, \quad \vartheta_1^\pm = \vartheta_0^\pm - \beta^\pm, \quad \vartheta_2^\pm = \vartheta_0^\pm + \beta^\pm, \\ |a_{10}^\pm| &= |a_{20}^\pm|, \quad |a_{10}^-| = |a_{10}^+|, \quad a_{11}^\pm = a_{21}^\pm = a_{11} = a_{21} = 0,\end{aligned}$$

where $\beta^\pm$ is obtained by substituting $a_{10}^\pm$ and a_{10}^- ($i=1,2$) respectively into the expression for β .

Thus the wave functions of the solution and the corresponding eigenvalues of the energy are written in the form

$$\left. \begin{aligned}E_{n(n_s)}^+ &= \vartheta_1^+ + \sum_s \hbar\omega_s \left(n_s + \frac{1}{2}\right) + \frac{1}{2} \sum_s \hbar\omega_s \xi_{s1n}^2 (a_{10}^+ a_{20}^+), \\ \Psi_{n(n_s)}^+ &= \frac{c}{\sqrt{2}} (\Phi_{10} - \Phi_{01}) \prod_s f_{n_s}(\xi_s - \xi_{s1n}^+),\end{aligned} \right\} \quad (22)$$

$$\left. \begin{aligned}E_{n(n_s)}^- &= \vartheta_1^- + \sum_s \hbar\omega_s \left(n_s + \frac{1}{2}\right) + \frac{1}{2} \sum_s \hbar\omega_s \xi_{s1n}^2 (a_{10}^- a_{20}^-), \\ \Psi_{n(n_s)}^- &= \frac{c}{\sqrt{2}} (\Phi_{10} + \Phi_{01}) \prod_s f_{n_s}(\xi_s - \xi_{s1n}^-).\end{aligned} \right\} \quad (23)$$

It follows from (22) and (23) that $(\Psi_{1\lambda(n_s)}^+ \cdot \Psi_{1\lambda(n_s)}^-) = 0$, where the magnitude of the splitting is determined by the expression

$$\begin{aligned}\Delta E &= E_{n(n_s)}^+ - E_{n(n_s)}^-, \\ &= V_{120} + \frac{1}{2} \sum_s \hbar\omega_s [\xi_{s1n}^2 (a_{10}^+ a_{20}^+) - \xi_{s1n}^2 (a_{10}^- a_{20}^-)].\end{aligned}\quad (24)$$

The second case can occur for like molecules which occupy nonidentical sites in the solvent (different energy of interaction with the solvent), or for molecules of nearly the same chemical composition which have almost identical energy spectra and interact in approximately the same way with the solvent. The condition $(A_I - A_\lambda)^2 \ll V_{120}^2$ can also be fulfilled sometimes for molecules with different energy spectra, but only for certain values of the quantum numbers l and λ . For these values of l and λ , the structure of the absorption spectrum of the impurity centers differs from the structures of spectra for other l 's and λ 's, as will be shown below. Then $(A_I - A_\lambda)^2 \ll V_{120}^2$ equation (19) gives us

$$\vartheta_0^\pm = \frac{1}{2} (A_I + A_\lambda) \pm |V_{120}| \pm \frac{(A_I - A_\lambda)^2}{8|V_{120}|}.$$

Substituting these energy values in the first of equations (17), we obtain expressions for the amplitude ratios,

$$\begin{aligned}\frac{a_{10}^+}{a_{20}^+} &= \frac{V_{120}}{|V_{120}|} \left\{ 1 - \frac{A_\lambda - A_I}{2|V_{120}|} - \frac{(A_I - A_\lambda)^2}{8|V_{120}|} \right\}, \\ \frac{a_{10}^-}{a_{20}^-} &= -\frac{V_{120}}{|V_{120}|} \left\{ 1 - \frac{A_I - A_\lambda}{2|V_{120}|} - \frac{(A_I - A_\lambda)^2}{8|V_{120}|} \right\}.\end{aligned}$$

Making further use of the additional condition, a_{10}^+ and a_{10}^- can be found and then corrections to the energies and amplitudes can be determined by formulas (20). It is easy to see that in the general case $|a_1^+| \neq |a_2^+|$, $|a_1^-| \neq |a_2^-|$. Consequently the wave functions and eigenvalues for the energy of the solution are written in the form

$$\left. \begin{aligned}E_{n(n_s)}^+ &= \vartheta_1^+ + \frac{1}{2} \sum_s \hbar\omega_s \left(n_s + \frac{1}{2}\right) + \frac{1}{2} \sum_s \hbar\omega_s \xi_{s1n}^2 (a_{10}^+ a_{20}^+), \\ \Psi_{n(n_s)}^+ &= \frac{c}{\sqrt{2}} (\Phi_{10} - \chi_1 \Phi_{10}) \prod_s f_{n_s}(\xi_s - \xi_{s1n}^+),\end{aligned} \right\} \quad (25)$$

$$\left. \begin{aligned}E_{n(n_s)}^- &= \vartheta_2^- + \sum_s \hbar\omega_s \left(n_s + \frac{1}{2}\right) + \frac{1}{2} \sum_s \hbar\omega_s \xi_{s1n}^2 (a_{10}^- a_{20}^-), \\ \Psi_{n(n_s)}^- &= \frac{c}{\sqrt{2}} (\Phi_{10} + \chi_2 \Phi_{10}) \prod_s f_{n_s}(\xi_s - \xi_{s1n}^-),\end{aligned} \right\} \quad (26)$$

where χ_1 and χ_2 are positive values close to unity (if $A_I > A_\lambda$, then $\chi_1 < 1$, $\chi_2 > 1$).

Finally, let us consider the third case, assuming for the sake of specificity that $A_I > A_\lambda$. Equation (19) gives us:

$$\vartheta_0^+ = A_I + \frac{V_{120}^2}{A_I - A_\lambda},$$

$$\vartheta_0^- = A_\lambda - \frac{V_{120}^2}{A_I - A_\lambda},$$

with

$$\frac{a_{10}^+}{a_{20}^+} = \frac{V_{120} (A_I - A_\lambda)}{V_{120}^2},$$

$$\frac{a_{10}^-}{a_{20}^-} = -\frac{V_{120}}{A_I - A_\lambda} \left[1 - \frac{V_{120}^2}{(A_I - A_\lambda)^2} \right].$$

We can determine the corrections to the energies and amplitudes a_{10} by making use of (20) in the same way as in the previous case. It is easy to see that in this case $|a_1^+| \gg |a_2^+|$, $|a_1^-| \ll |a_2^-|$. Consequently, the eigenvalues of the energy of the solution and the corresponding wave functions will have the form of (25) and (26), but $\chi_1 \ll 1$ and $\chi_2 \gg 1$. In the first case the excitation will be localized at the first molecule for all practical purposes (the additional excitation at the second molecule is small). In the second case, the excitation will be practically localized at the second molecule.

THE ABSORPTION OF LIGHT BY BINARY SOLUTIONS

Let us now deal with the polarization of quantum transitions under the action of light when the solution goes from the ground state $\Psi_{0(n_s)}$ to excited states $\Psi_{1\lambda(n_s)}^\pm$. As is known,¹² the probability of such a transition is proportional to

$$\sum_{[n_s]} \left| \int \Psi_{1\lambda(n_s)}^\pm \Psi_{0(n_s)} d\tau \right|^2 \cos^2 \vartheta, \quad (27)$$

where ϑ is the angle between the polarization direction of the absorbed light wave and the direction of the mean dipole moment of the transition; the sum over $[n_s]$ stands

for a summation over all sets of n' in final states associated with transitions in which the energy $\hbar\omega_{\pm} = E_{1\lambda(n_s)}^{\pm} - E_{0(n_s)}$ is absorbed; the bar over the sum indicates an average over all initial states. Substituting the expression for $\Psi_{1\lambda(n_s)}$ from (22)-(26) into (27) we find that the two matrix elements of the transition correspond respectively to the two states of the solution.

$$\left. \begin{aligned} m_1 &= \frac{1}{\sqrt{2}} \prod_i M_{n_s, n_s}^{n_i, 0} \left[a_1^+ \int \varphi_1^* \varphi_1^0 d\tau_1 + a_2^+ \int \varphi_2^* \varphi_2^0 d\tau_2 \right] = a_1^+ \varphi_1 + a_2^+ \varphi_2, \\ m_2 &= \frac{1}{\sqrt{2}} \prod_i M_{n_s, n_s}^{n_i, -} \left[a_1^- \int \varphi_1^* \varphi_1^0 d\tau_1 + a_2^- \int \varphi_2^* \varphi_2^0 d\tau_2 \right] = a_1^- \varphi_1 + a_2^- \varphi_2. \end{aligned} \right\} \quad (28)$$

The integrals which enter these expressions are independent of the energy of interaction between impurity centers, but as was pointed out above, the coefficients $a_i^{\pm}$ preceding the integrals depend on the relationship between the interaction energy of the impurity centers and the difference of their "energy" levels A_1 and B_{λ} . Therefore, corresponding to the three cases of this relationship that were previously considered we will also have three different values for the matrix elements m_1 and m_2 which will correspond to different absorption spectra.

In the first case, when $A_1 = A_{\lambda}$, the coefficients $a_i^{\pm}$ are equal in modulus and differ only in sign. According to (28) the resultant matrix elements will be the sum and difference of the matrix elements of the transitions in the impurity centers (Fig. 1a). It is easy to see that these matrix elements considered as vectors are mutually perpendicular, so that the absorption spectrum of the solution must be sharply polarized* when the electromag-

*If the pairs of impurity molecules are oriented identically in the solvent and if the pairs are identically "deformed" but oriented in several directions then the spectrum of the solution will appear as the superposition of the spectra from the pairs of each direction (in this case the sharp polarization will be absent).

netic field intensity vector of the light wave is appropriately oriented, in which case the spacing between polarized components is $|E_{1\lambda(n_s)}^+ - E_{1\lambda(n_s)}^-|$. If the oscillator strength is 0.03-0.1, this interval can approach 100-300 cm^{-1} , respectively (Fig. 1b). We note that the values of the matrix elements $V_{120}[\varphi_1^* \varphi_2^0 \varphi_1^0 \varphi_2^0]$ which essentially determine the degree of splitting will be different for a purely electronic transition and the various electron-vibrational transitions. For this reason it can also be expected, particularly when the purely electronic transition shows very little splitting, that the splitting will not be observed experimentally.* The matrix element V_{120}

*In this case and also when the degree of splitting is less than $\hbar\omega_s$ ($s = 1, 2, \dots$) the adiabatic method is impracticable and it is impossible to draw any kind of conclusions about the shape of the absorption band. The degree of splitting and the absorption can be similarly estimated^{13, 14} when the constitution of the solution is known.

can have a larger value for certain electron-vibrational transitions, which in turn leads to splitting of a sufficient degree to be observed experimentally.

The sharp polarization will not be present if the polarization vector of the light wave forms an angle $\theta \neq 0$ with the resultant dipole moment of the transition. When the polarization vectors of the light waves are mutually perpendicular, bands (lines) will be observed in the absorption spectra. Generally speaking, these will have

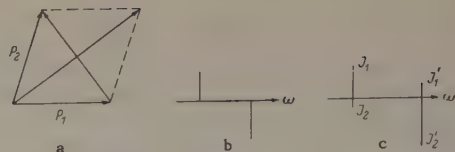


Fig. 1

different intensities for transitions to the states $E_{1\lambda(n_s)}^+$ and $E_{1\lambda(n_s)}^-$ (Fig. 1c). The ratio of intensities of lines of the same frequency for the two different polarizations will be equal to

$$\frac{J_1(\omega_1)}{J_2(\omega_1)} = \cot^2 \theta, \quad \frac{J_1'(\omega_2)}{J_2'(\omega_2)} = \tan^2 \theta$$

corresponding to the two possible transitions. Hence we find that the intensities of the split components are connected by the relationship

$$\frac{J_1(\omega_1) \cdot J_2'(\omega_2)}{J_2(\omega_2) \cdot J_1'(\omega_1)} = 1.$$

In the second case, when $(A_1 - A_{\lambda}) \ll V_{120}$, the ratios $a_1^{\pm}/a_2^{\pm}$ are different from unity, and generally speaking the matrix elements are not perpendicular. Consequently, sharp polarization will not be observed at such orientations of the light wave polarization vector. Maximum polarization can be attained only if the orientation of the polarization vector is changed so that it is parallel to one of the vectors m_1 or m_2 . For example, if the polarization vector is parallel to m_1 , then

$$\frac{J_2(\omega_1)}{J_1(\omega_1)} = 0, \quad \frac{J_2'(\omega_2)}{J_1'(\omega_2)} = \cot^2 \alpha \approx \frac{1}{a^2}.$$

Thus the angle between the resultant momenta m_1 and m_2 can be determined experimentally from this. The form of absorption spectrum in this case is shown in Fig. 2.

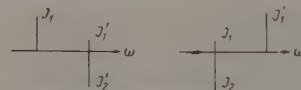


Fig. 2

In the third case, when $(A_1 - A_{\lambda})^2 \gg V_{120}^2$, the ratios $a_1^{\pm}/a_2^{\pm}$ are appreciably different from unity and the integrals entering into (28) also differ for the two different impurity centers. Thus the mutual perpendicularity of the vectors m_1 and m_2 will be encountered as an exception. In the general case the vectors m_1 and m_2 will not be perpendicular, and sharp polarization of components of the spectrum will not be observed at any orientation of the electromagnetic field intensity vector of the light waves. This vector can be rotated to make it parallel to one of the vectors m_1 or m_2 , but only one of the lines will be sharply polarized, whereas the second will be depolarized.

It can be expected that the luminescence spectra in all three cases will also be different. In the first case, with the transition from $E_{1\lambda(n_s)}^+$ and $E_{1\lambda(n_s)}^-$ to the ground state, the luminescence lines which correspond to the initial absorption lines will be sharply polarized, but because of radiationless transitions the blue line of the pair will be less intense than the red. In the second and third cases the luminescence spectra will be depolarized.

The relationship between the intensities of the first red and violet luminescence lines is determined in the general case by the relationship between the probability

a radiationless transition between $E_{1A(g)}^-$ and $E_{1A(g)}^-$ and the probability of thermal transfer from the lower of these levels to the higher (calculation of such transitions can be carried out only in a very rough approximation).

The shapes of absorption and luminescence bands, as well as the dispersion curve in the region of impurity absorption, can be calculated as in refs. 5 and 6; i.e., the results obtained there can be carried over directly to the present case of binary solutions. We only point out that if the absorption bands are broad and the separation small, they cannot be resolved experimentally. Consequently each of the bands will behave as was indicated in ref. 6; however, the over-all band will have other properties (in particular, at high temperatures its half-width will not increase in proportion to $\sqrt{T}$).

In conclusion our gratitude is expressed to A. S. Davydov for his discussions and interest in the work.

REFERENCES

1. Huang Kun and A. Rhys, *Proc. Roy. Soc.* **204**, 406 (1950).
2. B. Lax, *J. Chem. Phys.* **20**, 1752 (1952).

3. S. I. Pekar, *Zhur. Eksptl. i Teoret. Fiz.* **22**, 641 (1952).
4. A. S. Davydov, *Zhur. Eksptl. i Teoret. Fiz.* **24**, 197 (1953).
5. A. S. Davydov, *Nauk. Zapiski, Kiiv. Derzhav. Univ.* im T. G. Shevchenka **14**, No. 8, 5 (1955).
6. A. F. Lubchenko, *Ukrain. Fiz. Zhur.* **1**, 120-265-281 (1956); *Doklady Akad. Nauk, Ukr. SSR.* **3**, 253 (1956).
7. R. Kubo and Y. Toyozawa, *Prog. Theoret. Phys.* (Kyoto) **13**, 160 (1955).
8. A. S. Davydov, *Zhur. Eksptl. i Teoret. Fiz.* **24**, 397 (1953).
9. A. F. Lubchenko, *Izvest. Akad. Nauk SSSR Ser. Fiz.* **20**, 388 (1956).
10. A. I. Kitaigorodskii, *Doklady Akad. Nauk SSSR* **113**, 604 (1957).
11. A. I. Kitaigorodskii, *Kristallografiya* **2**, 465 (1957).
12. H. Keitler, "Kvantovaya teoriya izlucheniya." *Izd. Inostrannoi Lit. Moscow*, 1956. Translation of "Quantum Theory of Radiation," 3rd ed. Oxford Univ. Press, New York and London, 1954.
13. A. S. Davydov, "The Theory of Light Absorption in Molecular Crystals." *Izd. Akad. Nauk Ukrain. SSR, Kiev*, 1951.
14. D. Fox and O. Schnepp, *J. Chem. Phys.* **23**, 767 (1955).

INTERPRETATION OF THE ELECTRONIC SPECTRA OF PORPHYRINS ON THE BASIS OF SYMMETRY CONSIDERATIONS

K. N. Solov'ev (pp. 737-744)

Received 6 December 1960

An analysis of the existing experimental data on the spectroscopy of porphyrins, based on the methods of group theory, has been carried out. The characteristic absorption spectra of porphyrins in the visible region are interpreted as the result of the superposition of vibrations onto two electronic transitions. The essentially peculiar role of vibrations of the nuclei in the porphyrin system is stressed as a perturbing factor which allows a quasi-forbidden transition.

In their chemical nature, porphyrins are derivatives of porphin (Fig. 1, structural formula I). They possess characteristic absorption spectra consisting of a series of narrow bands, the spectra changing relatively little in going from one porphyrin to another. In the visible region there are four relatively weak bands; around 400 mμ there is located a very intense band (the "Soret band") which is characteristic not only for porphyrins, but also for all tetrapyrrole macrocycles (Fig. 2a). Up to the present, different points of view have existed with regard to the question of the origin of this type of spectrum. Meanwhile, the solution of this question will possibly be of great value for a detailed understanding of the optical properties of chlorophyll. At the present time, voluminous experimental data have been accumulated which enable us to discuss the problem of the interpretation of porphyrin spectra while bringing in the methods of group theory. The purpose of this work is this: starting from the existing experimental data and relying on only the most general concepts of theoretical spectroscopy, to determine the symmetry of the electronic and vibrational states which manifest themselves in the electronic spectra of porphyrins.

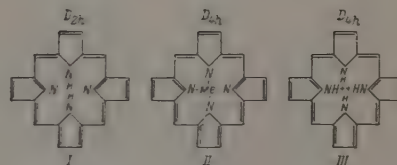


Fig. 1. Structural formulas of the molecules of porphin and its derivatives. I—porphin; II—metalloporphin; III—doubly charged porphyrin cation.

For the interpretation of porphyrin spectra, the following experimental facts are essential.

1. As a result of the introduction into a porphyrin molecule of a metal atom (Fig. 1, structure II) or of two extra protons in acid medium (Fig. 1, structure III), the four-banded spectrum goes over into a two-banded one, while the half-width of the Soret band diminishes¹ (Fig. 2). In ref. 2, on the basis of an investigation of the limiting polarization of fluorescence, it was established that these changes are associated with a transition from D_{2h} to D_{4h} .

symmetry, and also that the oscillators in the molecules of metalloporphyrins lie in the plane of the molecule.

2. The fluorescence spectra of porphyrins, which have two bands, are mirror-symmetric to the two longest-wavelength absorption bands (this is also true for the case of the two-banded absorption spectrum).*

*The only mention of the mirror symmetry of porphyrin spectra³ is thirty years old and is based on a purely qualitative observation. Specially conducted careful measurements have shown that for porphyrins the rule of mirror symmetry is not strictly fulfilled, but the deviations are generally not large.

The fluorescence spectrum does not depend on the wavelength of the exciting light.⁴

3. Bands I and III in the absorption spectrum correspond to linear oscillators oriented perpendicular to each other, and bands II and IV to "planar" oscillators having equal components along the coordinate axes in the plane of the molecule. In emission, the first band corresponds to a linear oscillator and the second to a planar one, all the oscillators lying in the plane of the molecule. These facts were established during a study of the dependence of the polarization of the fluorescence on the wavelength of absorption and emission.^{5*}

*The conclusion that the absorption bands II and IV are to be ascribed to planar oscillators is not contained in ref. 5 in explicit form, but it follows directly from the experimental data presented therein.

4. In the absorption spectrum of porphin, bands I and III are extremely weak (oscillator strength of the order of 0.01).⁶ In acid medium, band I is so weak that the spectrum appears to be one-banded and not two-banded, as in all other porphyrins.⁷ The spectrum of Mg-porphin⁸ has an analogous appearance. However, band I has a noticeable intensity⁹ (Fig. 3) in the spectrum of Cu-porphin.

5. The introduction of various side substituents into the porphin system does not show itself much in the general character of the spectrum; however, the intensities

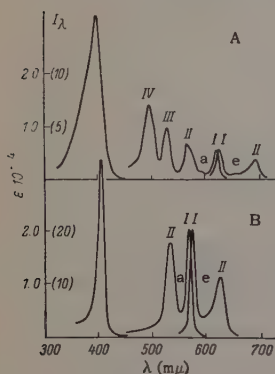


Fig. 2

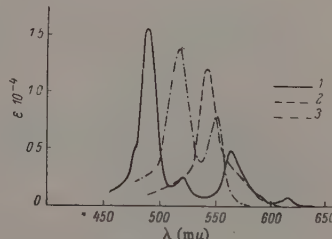


Fig. 3

Fig. 2. Absorption (a) and emission (e) spectra of mesoporphyrin IX dimethyl ether (A) and its zinc complex (B). Figures in parentheses (on the vertical axis) designate the intensity of the Soret band.

Fig. 3. Absorption spectra of porphin and its derivatives. Curve 1—porphin (according to ref. 6); curve 2—porphin in acid medium (according to ref. 7); curve 3—Cu-porphin (according to ref. 9).

of bands I and III prove to be by far the most sensitive to this influence, while the intensities of bands II and IV are practically unchanged (as also for the intensity of band II in the case of the two-banded spectrum). Band I of the two-banded spectrum behaves in this respect analogously to bands I and III.¹

From the experimental facts, two fairly evident but essential conclusions can be obtained at once. First, the optical processes in the molecules of porphyrins are brought about by transitions in the π -electron conjugated system (transitions of type $\pi \rightarrow \pi^*$, but not $n \rightarrow \pi^*$). If the transitions were of type $n \rightarrow \pi^*$, then, as is well known, the corresponding oscillators would be perpendicular to the plane of the molecule; this is associated with the antisymmetry of the π -electron orbitals with respect to the plane of the molecule and the symmetry of the n -orbitals with respect to this plane (see ref. 2). Second, the energy levels which manifest themselves in the porphyrin spectrum belong to one and the same molecule, and not to different tautomeric forms. This conclusion follows from the lack of dependence of the fluorescence spectrum on the exciting wavelength, and also from the presence of a characteristic polarization spectrum.

Group theory permits one to classify the electronic and vibrational states of molecules with respect to the transformation properties of the wave functions relative to different symmetry operations. Conjugated systems have the peculiarity that the π -electron orbitals are necessarily antisymmetric with respect to reflection in the plane of the molecule.* This limits the number of

*As is well known, the molecular orbital approximation, even though it is exceedingly rough, still permits one to obtain exact results with regard to the symmetry of the possible states.

possible orbitals, and consequently the number of states also. In particular, only the orbitals a_{1u} , a_{2u} , b_{1u} , b_{2u} , and e_g are possible for D_{4h} symmetry (see, for example ref. 10). In accordance with the rules of group theory, in order to determine the symmetry of the possible electronic states of a molecule, it is necessary to determine all possible direct products constructed in pairs from these orbitals. It appears as a result that, for D_{4h} symmetry, only the nondegenerate even states A_{1g} , B_{1g} , A_{2g} , and B_{2g} and the doubly degenerate odd state E_u are possible. On lowering of the symmetry to D_{2h} , the E_u state splits into two: B_{2u} and B_{3u} , and the even states change symbols— A_{1g} and B_{1g} go over into A_{1g} , and A_{2g} and B_{2g} into B_{1g} .

The unexcited electronic state of the molecules of porphyrins must be totally symmetric (A_{1g}), as also for other stable polyatomic molecules.* Hereafter we shall

*This conclusion, naturally, follows from the concept of molecular orbitals filled in the ground state by electron pairs with antiparallel spins (according to the Pauli principle). A certain confirmation of the correctness of this picture, namely, the filling of the electron shells, for the ground state of the molecules of porphyrins is provided by their diamagnetism.¹¹

start from this fundamental assumption. For dipole transitions* the following selection rules are obtained:

*Vavilov's method of polarization diagrams¹² is a convenient method of determining the nature of the elementary oscillators. Appropriate measurements have confirmed the expected dipole character of absorption and radiation in the molecules of porphyrins.

in absorption, only transitions to the degenerate E_u states (for D_{4h} symmetry) and to the B_{2u} and B_{3u} states (for D_{2h} symmetry) are allowed, the moments of the transitions $A_{1g} \rightarrow B_{2u}$ and $A_{1g} \rightarrow B_{3u}$ being mutually perpendicular.

It is altogether certain that the intense Soret band in the spectra of metalloporphyrins corresponds to an allowed transition; according to the selection rules for D_{4h} symmetry this band is to be assigned to the $A_{1g} \rightarrow E_u$ transition. The small change in the form of this band as the symmetry is lowered indicates that the states B_{2u} and B_{3u} which arise as a result of the splitting of the doubly degenerate state E_u lie close together in energy. Thus to the Soret band of neutral molecules of porphyrins there correspond two allowed transitions which have frequencies lying close together and which are oriented perpendicular to each other (this agrees with the results of the polarization measurements).

The low intensity of band I of porphin in acid medium suggests a forbidden character for the long-wavelength transition. In the porphin molecule, $g \rightarrow g$ transitions are forbidden; that is, transitions between nondegenerate states. Inasmuch as the prohibition imposed by Laporte's rule is strict, the assumption of a $g \rightarrow g$ transition contradicts the fact that band I of Cu-porphin has a noticeable intensity. The results of polarization measurements² show that the lower excited state of metalloporphyrin molecules and porphyrin cations is doubly degenerate. Consequently, the transition $A_{1g} \rightarrow E_u$, which is formally allowed by the selection rules for D_{4h} symmetry, may be unequivocally ascribed to band I of the two-band spectrum. In this case, the low intensity of band I cannot be explained by a symmetry prohibition, and one must bring in other considerations.

The low intensity of the absorption bands of porphyrins in the visible region was first explained by Simpson on the basis of the simplest free-electron model. In this model the electrons occupy $e^{1\varphi}$ orbitals, and the optical transitions take place between the orbitals $e^{+4\varphi}$ and $e^{+5\varphi}$. The quantum number 1, which characterizes the angular momentum of the electron, may then change by ± 1 (an allowed transition) or by ± 9 (a forbidden transition). Since the state with $L = \pm 9$ lies lower according to Hund's rule, it is just the long-wavelength transition which proves to be forbidden, which also explains the weakness of the long-wavelength absorption band.¹³ Without devoting oneself to an analysis of the views of various authors on this question, one may say that in cyclic conjugated systems there are possible causes which can greatly weaken transitions not forbidden by symmetry.

An analogous examination for D_{2h} symmetry shows that bands I and III correspond formally to the allowed electronic transitions $A_{1g} \rightarrow B_{2u}$ and $A_{1g} \rightarrow B_{3u}$, their relatively low intensity being brought about by the same causes as for D_{4h} symmetry. The choice of the symbol B_{2u} or B_{3u} for the lower excited state is arbitrary, since it depends on the choice of the coordinate system; it is essential that the transitions to the B_{2u} and B_{3u} states are oriented perpendicular to each other. Without loss of generality, one may consider that band I corresponds to the $A_{1g} \rightarrow B_{3u}$ transition, which is polarized along X. On elevation of the symmetry to D_{4h} , the transitions $A_{1g} \rightarrow B_{2u}$ and $A_{1g} \rightarrow B_{3u}$ fuse into the single transition $A_{1g} \rightarrow E_u$, which also explains the above-mentioned kinship of bands I and III with band I of the two-band spectrum.

The idea of the removal of degeneracy as the cause

of the transition from a two-band spectrum to a four-band one was first expressed by Platt,¹⁴ who started basically from the results of approximate quantum-mechanical calculations (LCAO method). At first glance, the assumption of the degenerate character of the excited electronic states of porphyrins contradicts the well-known Jahn-Teller theorem, according to which degenerate electronic states are impossible in nonlinear molecules (they are split under the influence of the vibrations of the nuclei).¹⁵ However, as has been shown, the presence of degeneracy in the molecules of porphyrins has been experimentally demonstrated; from the point of view of the Jahn-Teller theorem, this denotes that the splitting is small (less than the half-width of the band).² It must be noted that the polarization spectrum predicted by Platt on the assumption of the vibrational character of bands II and IV differs sharply from the experimental one. A detailed examination, presented below, shows that the cause of this discrepancy is not the incorrectness of the interpretation of the electronic transitions but the failure to take account of the specific role of vibrational motion in the molecules of porphyrins.

The fulfillment of the mirror-symmetry rule for the spectra, and the mirror symmetry of the variations in polarization relative to the frequency of the purely electronic transition,⁵ compel us to suppose that bands II in absorption and emission are brought about by the excitation of vibrations. This contention may also, with sufficient basis, be extended to band IV. The necessity for representing band II by a planar oscillator indicates the presence of the two equally probable transitions $A_{1g} \rightarrow \bar{B}_{2u}$ and $A_{1g} \rightarrow \bar{B}_{3u}$ which are responsible for this band (the bar over the symbol denotes an electronic-vibrational wave function). A simple analysis of the direct products for the D_{2h} group shows that such states may arise on excitation of the vibrations α_{1g} and β_{1g} (Greek letters denote a vibrational wave function). Actually, we have previously ascribed the symmetry B_{3u} to the lower excited electronic state; excitation of the vibration α_{1g} will give the state $\bar{B}_{3u}$ ($B_{3u} \cdot \alpha_{1g} = \bar{B}_{3u}$), and excitation of the vibration β_{1g} will give the state $\bar{B}_{2u}$ ($B_{3u} \cdot \beta_{1g} = \bar{B}_{2u}$). Analogously, the equally probable transitions $A_{1g} \rightarrow \bar{B}_{2u}$ and $A_{1g} \rightarrow \bar{B}_{3u}$, brought about by superposition of the vibrations α_{1g} and β_{1g} on the state B_{2u} ($B_{2u} \cdot \alpha_{1g} = \bar{B}_{2u}$; $B_{2u} \cdot \beta_{1g} = \bar{B}_{3u}$), must correspond to band IV. In emission, the equally probable transitions $B_{3u} \rightarrow \bar{A}_{1g}$ and $B_{3u} \rightarrow \bar{B}_{1g}$, oriented perpendicular to each other and brought about by superposition of the same vibrations α_{1g} and β_{1g} on the ground state ($A_{1g} \cdot \alpha_{1g} = \bar{A}_{1g}$; $A_{1g} \cdot \beta_{1g} = \bar{B}_{1g}$), must correspond to band II.

Thus, in the electronic spectra of porphyrins, there are manifested the totally symmetric vibration α_{1g} , which does not change the direction of the oscillator, and the nontotally symmetric vibration β_{1g} , which brings about a transition oriented perpendicularly to the purely electronic one. The equality of the X- and Y-components in the vibrational bands, which follows from experiment, denotes that these vibrations manifest themselves in equal measure in the spectrum. It is known, however, that the application of the Franck-Condon principle to the case of polyatomic molecules requires the predominant appearance of totally symmetric vibrations in the spectrum. For the elimination of this contradiction, it is necessary to take account of the quasi-forbidden character of the electronic transitions in the molecules of porphyrins.

As is well known, the vibrational structure of for-

bidden transitions arises in consequence of the dependence of the matrix element of the dipole moment of the transition on the coordinates of the nuclei.^{16,17} For small displacements of the nuclei, the moment of the transition may be broken down into a series in the normal coordinates

$$D = D_0 + \sum_i D_i q_i + \sum_{ik} D_{ik} q_i q_k + \dots \quad (1)$$

where the q_i 's represent the normal coordinates which give the magnitude of the displacements in the i -th normal vibration. If $D_0 = 0$, then vibrational bands appear in the spectrum in consequence of the superposition of nontotally symmetric vibrations on account of the $D_i q_i$ terms which determine the intensity and polarization of the transitions; i.e., the nontotally symmetric vibrations, by breaking down the symmetry of the equilibrium configuration, remove the prohibition. In order for the coefficients D_i not to reduce to 0, the fulfillment of the strict selection rule

$$\int \psi_{\text{el.}}^* \psi_{\text{vib.}}^* D \psi_{\text{el.}} \psi_{\text{vib.}} d\tau_{\text{el.}} d\tau_{\text{vib.}} \neq 0. \quad (2)$$

is necessary.

Starting from these general considerations, let us examine how vibrations manifest themselves in the spectra of porphyrins. In this case D_0 does not equal 0, but it is very small, especially for porphin. Consequently, the $D_i q_i$ terms must play an extremely important role; i.e., the mechanism of the superposition of vibrations does not essentially differ from the case of strictly forbidden transitions: vibrations which disrupt the equilibrium configuration perturb the system and remove the prohibition, the criterion for removal of the prohibition being contained in the strict selection rule (2). The vibrations α_{1g} and β_{1g} which interest us satisfy this criterion by the conditions of their selection. Thus the fact that the totally symmetric vibration α_{1g} removes the prohibition—i.e., plays the role of a perturbing factor—is an essential peculiarity of porphyrins, brought about by the quasi-forbidden character of the electronic transitions (the transitions are formally allowed by symmetry). It appears most probable that this role is filled not by the "breathing" vibrations but by the vibrations depicted in Fig. 4, nontotally symmetric for D_{4h} symmetry and totally symmetric (α_{1g}) for D_{2h} symmetry. Of the possible types of β_{1g} vibrations, the appearance in the spectrum of the vibrations depicted in Fig. 4 and similar in form to the α_{1g} vibrations is more probable. We note that, according to Craig,¹⁸ the e_g^+ vibrations which remove the prohibition in the benzene molecule have a similar form.

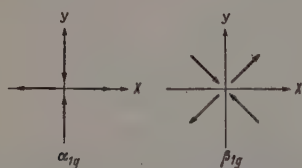


Fig. 4. Probable forms of the vibrations which manifest themselves in the electronic spectra of porphyrins.

We may now estimate the intensities of the X- and Y-components in band II of the absorption spectrum of a porphyrin (in the calculation we assume that the electronic

transition is polarized along X; i.e., that $D_{0X} = D_0$; $D_{0Y} = D_{0Z} = 0$):

$$X = \left(D_0 \int \psi_{\text{el.}}^* \psi_0^* d\tau_{\text{vib.}} + D_{\alpha_{1g}} \int \psi_{\text{el.}}^* q_{\alpha_{1g}} \psi_0^* d\tau_{\text{vib.}} \right)^2; \quad (3)$$

$$Y = \left(D_{\beta_{1g}} \int \psi_{\text{el.}}^* q_{\beta_{1g}} \psi_0^* d\tau_{\text{vib.}} \right)^2. \quad (4)$$

Analogous expressions are obtained for band IV (X and Y change places) and for band II in the emission spectrum. There is every reason to neglect the first member of the X-component, not only on account of the smallness of D_0 but also on account of the weakness of the vibrational structure of the allowed transitions in porphyrins and related compounds ($\int \psi_{\text{el.}}^* \psi_0^* d\tau_{\text{vib.}}$ is also small). This means that the conclusion concerning the predominant appearance of totally symmetric vibrations in the spectra of polyatomic molecules has no force in the case of porphyrins. In passing, we have also explained the smallness of the changes in bands II and IV on introduction of side substituents: to a certain approximation, the magnitude of D_0 does not enter into the expression for the intensity, and small changes in D_0 will not affect the intensity of a vibrational band.

Thus the assumption of the vibrational origin of bands II and IV in the spectra of porphyrins is in agreement with experiment. The similarity in the expressions obtained for the X- and Y-components makes understandable the peculiarities of the oscillator representation of the electronic-vibrational transitions in this case.

A quantitative explanation of the equality of the intensities of the X- and Y-components in bands II and IV and in band II in fluorescence is impossible at the present time, since the exact form of the dependence of D on the vibrational coordinates is unknown. However, for a qualitative explanation, one may draw on the results of an estimate of the intensity of forbidden transitions, as obtained by Herzberg and Teller by simple perturbation theory.¹⁶ According to this estimate, in order for a vibration to remove a prohibition, it is necessary not only that condition (2) be fulfilled, but also that there be present, near the level to which transition is forbidden, a perturbing level of appropriate symmetry, transition to which is allowed. Then the intensity of the band produced by the $D_i q_i$ terms will be proportional to the quantity $[1/(E_s - E)]^2$, where E is the energy of the level, from transition to which the prohibition is being removed, and E_s is the energy of the perturbing level. In the case of porphyrins, the levels of the Soret band (B_{2u} and B_{3u}) are such perturbing levels. Apparently, inasmuch as the intensities of the X- and Y-components are determined only by the $D_i q_i$ terms, the equality of these components may be brought about by the fact that the corresponding perturbing levels have approximately equal energy (ΔE_s is the same). The well-known fact that band IV is more intense than band II in all porphyrins is an oblique confirmation of this viewpoint (band IV is closer to the Soret band; $\Delta E_s = 0.7$ eV for it as against 1.1 eV for band II).

The examination just carried out enables us to interpret the absorption spectra of porphyrins in the visible region in the following way. Bands I and III correspond to separate electronic transitions; bands II and IV correspond to electronic-vibrational transitions, the totally and nontotally symmetric vibrations manifesting themselves in the spectrum in equal measure. In accordance with everything set forth above, the level diagram

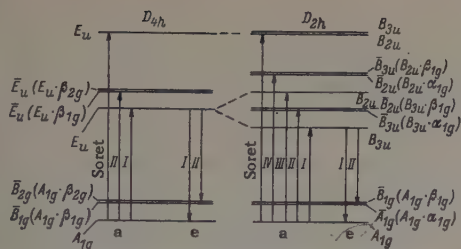


Fig. 5. Energy level diagram for the molecule of a porphyrin (a—absorption, e—emission). The symmetry types of the electronic states are characterized by the standard symbols of group theory. Greek letters denote the symmetry types of the superimposed vibrations; symbols with a bar above denote the symmetry types of the electronic-vibrational wave functions. Broken lines illustrate the splitting of degenerate levels when the symmetry is lowered.

analysis of the experimental data.

The author considers it his pleasant duty to express his sincere gratitude to academicians M. A. El'yashevich, A. N. Sevchenko, and B. I. Stepanov of the Academy of Sciences of the Byelorussian SSR for their constant interest in the work and their valuable comments in discussion of the results obtained.

REFERENCES

1. H. Fischer and H. Orth, "Die Chemie des Pyrrols," 1st ed., Vol. II, p. 579, Leipzig, 1937.
2. A. N. Sevchenko, G. P. Gurinovich, and K. N. Solov'ev, Doklady Akad. Nauk SSSR 128, 510 (1959); Opt. i Spektr. 10, 750 (1961), Optics and Spectroscopy, 10, 396 (1961).
3. H. Hellström, Z. physik. Chem. B12, 353 (1931).
4. P. Pringsheim, "Fluorescence and Phosphorescence," p. 339. Izd. Inostrannaya Lit., Moscow, 1951. Interscience, New York and London, 1949.
5. A. N. Sevchenko, G. P. Gurinovich, and K. N. Solov'ev, Doklady Akad. Nauk SSSR 133, 564 (1960). Soviet Phys.-Doklady 5, 808 (1961).
6. C. Rimington, S. F. Mason, and O. Kennard. Spectrochim. Acta 12, 65 (1958).
7. A. Stern and H. Wenderlein, Z. physik. Chem. A175, 405 (1936).
8. U. Eisner and R. P. Linstead, J. Chem. Soc. 3749 (1955).
9. A. Stern, H. Wenderlein, and H. Molvig, Z. physik. Chem. A177, 40 (1936).
10. H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, J. Chem. Phys. 18, 1174 (1950).
11. F. Haurowitz and H. Kittel, Ber. 66, 1046 (1933).
12. S. I. Vavilov, Zhur. Eksptl. i Teoret. Fiz. 10, 1363 (1940).
13. W. T. Simpson, J. Chem. Phys. 17, 1218 (1949).
14. J. R. Platt, Radiation Biol. 3, 71 (1956).
15. H. A. Jahn and E. Teller, Proc. Roy. Soc. A161, 220 (1937).
16. G. Herzberg and E. Teller, Z. physik. Chem. B21, 410 (1933).
17. H. Spöner and E. Teller, Revs. Modern Phys. 13, 75 (1941).
18. D. P. Craig, J. Chem. Soc. 59 (1950).
19. E. Rabinowitch, "Photosynthesis," Vol. 2. Izd. Inostrannaya Lit., Moscow, 1953. Interscience, New York and London, 1945.
20. S. L. Matlow, J. Chem. Phys. 23, 673 (1955).

ABSORPTION BY VAPORS OF ORGANIC COMPOUNDS II. Bibenzyl and Stilbene

O. P. Kharitonova (pp. 745-749)

Received 7 July 1960

The absorption spectra of bibenzyl and stilbene vapors have been investigated at various absorbing thicknesses and different temperatures. The absorption coefficients and oscillator strength in the first electronic transition have been determined. A comparison with the spectra of solutions of these compounds in ethyl alcohol and of crystals at 20°K has been carried out.

BIBENZYL

The spectra of bibenzyl vapor have been little studied.¹⁻³ In the present work, the absorption spectra of bibenzyl vapor have been obtained at thicknesses of 10, 50, and 100 cm and temperatures from 18 to 130°C. The experimental procedure has been previously described.^{4,5} Carefully purified bibenzyl was used for the study (no stilbene impurity was found in its spectra under the conditions indicated above).

At a layer thickness of 10 cm and a temperature of 130°C (i.e., at high vapor pressures, as determined from the tabular data of ref. 6), the absorption spectrum obtained for bibenzyl vapor consists of a series of broad diffuse bands with a washed-out red edge and a sharper violet one. The spectrum is located in the region 37,400-40,550 cm⁻¹; the bands are of low intensity, and their rotational structure is not resolved. The next absorption region begins at the frequency $\nu = 44,500$ cm⁻¹. Going over to a layer thickness of 50 cm made it possible to obtain a spectrum at a lower temperature. Its appearance was somewhat changed in the process. Thus at 90°C the bands become narrower, on account of which their intensity increases and the violet edge becomes sharper. At 75°C, narrow lines with a width of 5-10 cm⁻¹ appear on a background of diffuse bands, starting from the ultraviolet edge. The fall-off in intensity toward the red becomes more abrupt. Increase in the length of the absorbing layer to 100 cm made it possible to lower the vapor pressure still further (through lowering of the temperature to 18°C); however, even at 40°C the background completely disappears from the spectrum, and only the fine lines belonging to the purely electronic or electronic-vibrational transitions remain. Lowering of the temperature to 18°C does not change the appearance of the spectrum, but only lowers the intensity of the absorption lines somewhat. In Table 1 are presented the results of measurements of the positions of the maxima of the spectral lines at 40°C and a layer thickness of 100 cm, and an analysis of them is given.

Table 1

No.	$\Delta\nu$ (cm ⁻¹)	ν (cm ⁻¹)	Analysis	Intensity	No.	$\Delta\nu$ (cm ⁻¹)	ν (cm ⁻¹)	Analysis	Intensity
1	37290	—180	—	—	11	38740	1270	—	vw
2	37410	—60	—	—	12	38846	1376	930 + 458	vw
3	37470	0	—	vs	13	38930	1460	930 + 520	vw
4	37928	458	—	w	14	39140	1670	930 + 745	w
5	37990	520	—	w	15	39190	1720	961 + 745	w
6	38215	745	—	m	16	39358	1888	930 + 961	vw
7	38400	930	—	s	17	39524	2054	930 + 1136	w
8	38431	961	—	s	18	40448	2978	930 × 2 + 1136	w
9	38604	1136	—	m	19	40540	3070	961 × 2 + 1136	vw
10	38656	1188	—	m					

Note symbols for band intensities: vs — very intense; s — intense; m — medium intensity; w — weak; vw — very weak.

If we take the frequency of the maximum of the first intense band, $\nu = 37,470$ cm⁻¹, as the frequency of the purely electronic transition, then it will combine with the following frequencies: 458, 520, 745, 930, 961, 1136, 1188, and 1270 cm⁻¹. From the spectrum obtained at a temperature of 90°C and a layer thickness of 50 cm, values of the absorption coefficients $\kappa(\nu)$ ¹³ were determined, and also the equivalent values of the effective absorbing diameter $\sigma(\nu)$ which characterizes the absorbing power of the molecule. This quantity is convenient for comparison of the spectra. From the curve of the function $\kappa(\nu)$, the value of the oscillator strength of the transition under study was calculated: $f = 0.005$. According to the absorption spectra of a solution of bibenzyl in ethyl alcohol at 20°K, $f = 0.006$.³

In Fig. 1 is presented a comparison of the absorption spectra of bibenzyl vapor at a layer thickness of 50 cm and a temperature of 90°C and of a solution of bibenzyl in ethyl alcohol at 20°K. For superposition of the spectra, the solution spectrum had to be displaced by 180 cm⁻¹ toward the ultraviolet (to reach coincidence of the maxima of the first bands, which are assigned to the purely electronic transition). In the same figure is presented the absorption spectrum of a bibenzyl monocrystal (in arbitrary units) taken from ref. 7, and at the bottom is shown a diagram of the vapor spectrum at a layer thickness of 100 cm and 40°C. Here the first band of the crystal spectrum has been displaced by 176 cm⁻¹ toward the ultraviolet.

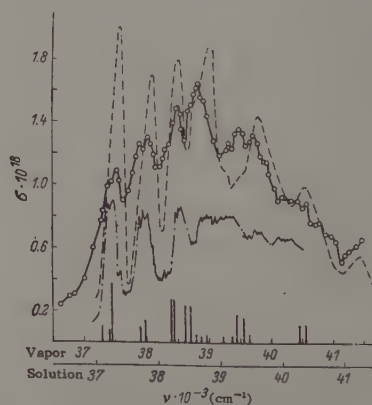


Fig. 1. Absorption spectra of bibenzyl in different states of aggregation. Solid line—vapor at $t = 90^\circ\text{C}$; broken line—solution in ethyl alcohol at 20°K; dot-and-dash line—crystal (b-component) at 20°K. Below—diagram of the vapor spectrum at $t = 40^\circ\text{C}$.

Photometry of the fine lines obtained at a temperature of 40°C would be to no purpose, since in our arrangement there were no data on the vapor pressure P at this temperature. Extrapolation of the $P(t)$ curve introduces a large error in the determination of P , and consequently in the determination of the quantity N —the number of molecules—on which the value of the oscillator strength depends. Nevertheless, for an approximate estimate of the value of the oscillator strength, we measured photometrically the first three lines entering into the first band of the spectrum obtained at 40°C. It turned out that the total oscillator strength of these three lines was equal to 1.47×10^{-4} , while for the first band at 90°C $\sigma = 6.85 \times 10^{-4}$. Such an agreement may be considered satisfactory if one takes into account the inexactness of the determination of P .

Similarity of the spectra is observed in all states of aggregation: even in the broad vapor bands one can note a vibrational structure which also exists in the crystal spectrum. At the same time, there is no structure in the solution spectrum, probably on account of the diffuseness of the bands.

According to existing theory,⁷ the π -electronic states of the bibenzyl molecule have a similarity to the π -electronic states of the toluene molecule, in consequence of which the spectra of the two compounds must be similar. Actually, on comparison of the absorption spectra of bibenzyl vapor at 40°C and a layer thickness of 100 cm and of toluene vapor at a thickness of 50 cm and a temperature of -30°C, one can see a striking similarity of these spectra, which breaks down somewhat as one progresses into the ultraviolet region. Beside the general similarity in the character of the spectra, one also observes an agreement in the values of the vibrational frequencies in the excited state. In Table 2 are presented the vibrational frequency values in the absorption spectra of bibenzyl and toluene vapors and crystals,^{7,8} and also the frequencies from Raman spectra¹⁰ corresponding to them. It can be seen from Table 2 that a great resemblance of the values of the vibrational spacings is observed in all cases (including the crystal spectra also). Such a striking similarity suggests the possible existence of thermo- and photoreactions which take place on heating or irradiation of the bibenzyl molecules. However, it has been shown by a number of authors¹⁰⁻¹³ that breakdown of the bibenzyl molecule into toluene molecules is possible only during an electric discharge through rarefied bibenzyl vapor at high carrier gas pressures (under these conditions dimerization of toluene molecules is also possible). In crystals at 20°K such a breakdown phenomenon has been observed by no one, but the similarity in the vibrational frequencies exists in this case also.

Thus the results obtained with respect to the bibenzyl spectra once again confirm the similarity of the π -elec-

tronic states of the two indicated molecules.

The value of the oscillator strength in toluene vapor is not known to us; however, the fact that continuous absorption appears at 120°C in the bibenzyl vapor spectrum at a layer thickness of 50 cm and at 10°C in the toluene spectrum at the same layer thickness indicates an absorption intensity which is greater in toluene in comparison with bibenzyl. Evidently the attachment of one benzene ring to another benzene ring through a CH_2 - CH_2 connecting link lowers the intensity of light absorption by the bibenzyl molecule.

STILBENE

This compound belongs to the class of strongly absorbing substances and has two isomers—*cis*- and *trans*-stilbene. The *cis*-form is unstable and decomposes easily. In the present work, the absorption spectrum of *trans*-stilbene vapor, obtained at a layer thickness of 50 cm and at temperatures from 50 to 80°C, was investigated. It was established that stilbene absorption depends sharply on the vapor pressure. Thus, at a temperature of 80°C continuous absorption begins at a frequency of $32,200 \text{ cm}^{-1}$. On lowering the temperature to 75°C, a broad diffuse absorption band appears in the spectrum, which on further reduction of the temperature begins to divide into a series of narrower and likewise diffuse bands. The accuracy of measurement of the position of the maxima of these bands is rather low, and consequently only an approximate determination of the fundamental vibration frequency is possible (it equals 1300 cm^{-1}). On further lowering of the temperature, the absorption intensity begins to fall off sharply, and at 50°C complete transparency of the chosen absorbing layer sets in. For a layer thickness of 50 cm the most intense absorption sets in at a temperature of 71°C and occupies the region from 32,000 to $41,000 \text{ cm}^{-1}$.

The oscillator strength of the transition under study, computed from the integrated absorption curves, equals 0.74. In solution, according to Shpak's data,³ the oscillator strength equals 0.6; in the crystal, according to the data of Brodin,¹³ who obtained a value for the oscillator strength on the basis of the curves of the function $\kappa(\nu)$ for the *a*-component of the crystal only, $f = 0.13$. For the *b*-component, the value of f was calculated in ref. 13 from the dispersion curves and came to 0.64.

A comparison of the absorption spectra of the vapor

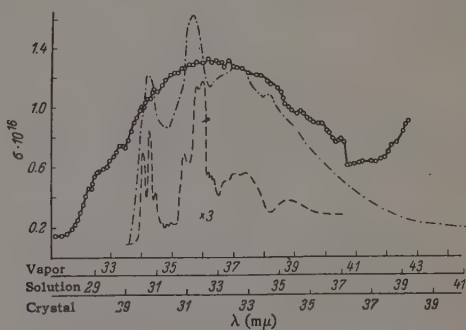


Fig. 2. Absorption spectra of stilbene in different states of aggregation. Solid line—vapor at $t = 71^\circ\text{C}$; broken line—crystal, *a*-component, at 20°K ; dot-and-dash line—solution in ethyl alcohol at 20°K .

Table 2

Bibenzyl			Toluene		
Vapor	Crystal	Ram.	Vapor	Crystal	Ram.
$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
458	444	476	456	457	463
	492	—		528	521
520	535	—		527	521
745	757	760		751	732
930	930	847		932	894
964	959	1002		964	977
1136	1139	1153		—	—
1188	1196	1200	1189	1190	1182
1270	1260	1343	—	—	—

Note symbols: Ram. — Raman spectrum. The frequencies $\Delta\nu$ are given in cm^{-1} .

at 71°C and a layer thickness of 50 cm, of solutions in ethyl alcohol at 20°K, and of the a-component of a stilbene single crystal, also at 20°K, is presented in Fig. 2. The superposition of the spectra was carried out in such a way that the first band in the crystal spectrum, which consists of three narrower bands, and a band in the vapor absorption spectrum were coincident. Then the "centers of gravity" of the spectra also coincide. Analogously, the

solution spectrum was also superimposed on the spectra just mentioned, for which it had to be shifted by 3330 cm⁻¹ toward the ultraviolet (the spectrum of the a-component of the crystal was shifted by 4480 cm⁻¹). Such a large shift indicates the great light-absorbing power of the stilbene molecule.

In conclusion, I express my thanks to A. F. Prikhod'ko for his constant attention to this work.

REFERENCES

1. Y. E. Purvis, *J. Chem. Soc.* **105**, 590 (1914).
2. A. Castill, *Bull. acad. roy. Belge* **12**, 498 (1926).
3. M. T. Shpak, *Kand. diss. (Dissertation)*, Kiev, 1955.
4. A. F. Prikhod'ko, *Zhur. Eksptl. i Teoret. Fiz.* **19**, 487 (1949).
5. O. P. Kharitonova, *Opt. i Spektr.* **5**, 29 (1958).
6. G. W. C. Kaye and T. H. Laby, "Tables of Physical and Chemical Constants and some Mathematical Functions." *Izd. Inostrannaya Lit., Moscow*, 1949. 12th ed., Longmans, New York, 1959.
7. R. Coffman and D. S. McClure, *Can. J. Chem.* **36**, 48 (1958).
8. V. L. Broude, *Opt. i Spektr.* **1**, 387 (1956).
9. Landolt-Börnstein *Phys.-Chem. Tabellen* **359**, 514 (1951).
10. I. Ambrush, *Uspekhi Khim.* **26**, 345 (1956).
11. M. Vacher and I. Lortie, *Compt. rend. acad. sci.* **236**, 1759 (1953).
12. G. A. Razuvaev and Yu. A. Ol'dekop, *Uchenye Zapiski Gor'kovsk. Univ. No. 17*, 171 (1951).
13. M. S. Brodin, *Ukrain. Fiz. Zhur.* **1**, 376 (1956).

INTRINSIC POLARIZATION OF THE FLUORESCENCE OF PORPHYRINS

G. P. Gurinovich, A. N. Sevchenko, and K. N. Solov'ev (pp. 750-758)

Received 13 July 1960

A study has been made of the intrinsic fluorescence of porphyrins in acid media, and of metalloporphyrins and porphyrins in neutral media. On the basis of the results obtained, conclusions have been drawn concerning the assignment of molecules of these compounds to D_{4h} and D_{2h} symmetry, and a structural model of these molecules has been suggested.

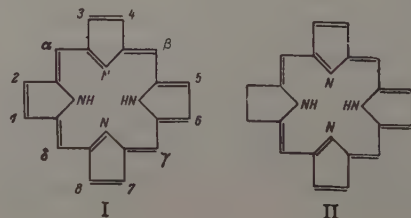
INTRODUCTION

The porphyrins are of great importance in many biological processes, and deserve careful study. It suffices to say that both chlorophyll and hemoglobin are porphyrins. The latter are also very interesting from the purely physical point of view, because their molecules are complex conjugated systems which have very characteristic spectra. There is as yet no satisfactory interpretation of these spectra, although there are some recent papers in which the spectral regularities observed in porphyrins are connected with symmetry properties. However, there is no generally accepted point of view regarding the symmetry of the porphyrins under various conditions. Therefore, the attempts at interpreting the spectra of porphyrins cannot be considered well founded.

It is thus necessary to study the molecular symmetry of the porphyrins experimentally. A convenient method for solving this problem is the method of intrinsic (limiting) polarization. It is known that it is not possible to represent highly symmetrical planar molecules by a single linear oscillator. The intrinsic polarization of luminescence from molecules having a symmetry higher than third order cannot exceed 1/7¹ (this corresponds to Jablonski's model of a two-dimensional oscillator²), whereas in the case of second order symmetry, it may reach 1/2 (which is the theoretical value for an ensemble of randomly oriented linear oscillators).

EXPERIMENTAL PROCEDURE

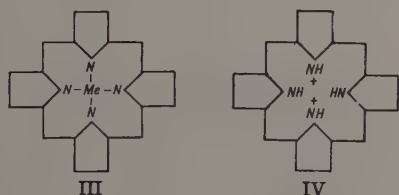
We studied the polarization of the fluorescence of porphyrins in an acid medium, and that of metalloporphyrins and porphyrins in a neutral medium. All of the compounds investigated were derivatives of porphin, the molecule of which contains four pyrrole rings connected by methine bridges (I). Strictly speaking, chlorophyll and pheophytin are derivatives of dihydroporphin (II). Besides the abovementioned hydrogenation of one of the pyrrole rings, a characteristic property of the structure of these molecules is the presence of an isopentane ring connecting carbon atoms γ and δ. The only feature which distinguishes protopheophytin from pheophytin-a is the fact that protopheophytin does not have a hydrogenated pyrrole ring (protopheophytin is a derivative of porphin, not of chlorin). In the tetrazaporphin molecule, there are nitrogen atoms instead of the CH-groups of the methine



bridges. Phthalocyanin can be considered a tetrabenzo-tetrazaporphin.

Porphin, which does not have side chains, would be the most interesting object for investigating the symmetry properties of molecules. However, the molecules of tetraphenylporphin and tetrazaporphin which we studied must have the same symmetry properties as the porphin molecule. Therefore, conclusions concerning the symmetry of the latter molecules must also apply to the porphin molecule. Unfortunately, tetraphenylporphin does not fluoresce in an acid medium, and this makes it impossible to study the symmetry of the positive ion by the intrinsic polarization method.

The porphyrins are capable of forming stable complex compounds with metals, the structure of which is similar to structure (III). In an acid medium, the porphyrin molecules acquire two protons, forming doubly-charged ions (IV).



Most of the compounds investigated were prepared by M. G. Gurevich in our laboratory. α -, β -, γ -, and δ -tetraphenylporphin were prepared by treating pyrrole with benzaldehyde in the presence of zinc acetate. The compounds were purified by chromatography and recrystallization. Protoporphyrin IX (dimethyl ester) was extracted from bovine blood by Grinstein's³ procedure. Mesoporphyrin (dimethyl ester) was obtained by reducing protoporphyrin with hydriodic acid in the presence of ascorbic acid.⁴ Protopheophytin was prepared by treating an extract of pumpkin seeds with concentrated hydrochloric acid, followed by chromatography on a sucrose column. The zinc complexes of the porphyrins were obtained by interaction of zinc acetate with the corresponding porphyrin in boiling pyridine. Mg-tetraphenylporphin was obtained by heating magnesium oxide and tetraphenylporphin in alkaline methanol in a sealed tube at 200°C. It was purified chromatographically.

Tetrazaporphin was obtained by decomposing Mg-tetrazaporphin in glacial acetic acid at room temperature.*

*The authors express their sincere gratitude to I. G. Tishchenko for synthesizing the Mg-tetrazaporphin, and to B. L. Kaller for supplying the protochlorophyll.

Highly viscous solutions are needed for the polarization measurements. The best solvent for this purpose is glycerin. It was found, however, that porphyrins are not soluble in neutral glycerin, but become soluble upon acidification. Castor oil was therefore used to obtain neutral porphyrin solutions of the necessary viscosity, whereas glycerin saturated with dry HCl ("acid glycerin") was used as the viscous acid medium. For the determination of the intrinsic polarization, the dependence of the degree of polarization on the viscosity of the solution was studied, the latter being varied over a fairly wide range by changing the temperature of the solution. The intrinsic polarization was obtained by using the Levshin-Perrin⁵ expression and extrapolating to infinite viscosity.

By its very nature, the intrinsic polarization method requires that the polarization measurements be made in the short-wavelength emission band, with excitation in the long-wavelength absorption band. This circumstance is very important in the case of the porphyrins, because their spectral bands are narrow, spaced fairly close to each other, and partially overlap, and the degree of polarization of the fluorescence depends greatly on the wavelength of both the excitation^{6,7} and the luminescence.⁸ All of these circumstances render the usual method of polarization measurement (the use of crossed filters) impractical for porphyrins. The need for separating the spectral ranges of the luminescence and the exciting light by at least a half-width of the spectral bands of the porphyrins (that is, about 15 m μ) makes it necessary to use two monochromators. The two-monochromator arrangement used has been described previously.⁸ In each case, the measurement of the intrinsic polarization was made in the short-wavelength luminescence band, with excitation in the long-wavelength absorption band. The sensitivity of the apparatus allowed us to work with slits whose spectral width did not exceed the half-width of the corresponding bands.

EXPERIMENTAL RESULTS

The spectra of the porphyrins and the metalloporphyrins in castor oil differ by only a slight shift of the bands (not exceeding 5 m μ) relative to the spectra of dioxane and benzene, which in turn agree well with the data in refs. 9 and 10. The spectra of the porphyrins in acid glycerin also differ only slightly from the spectra of solutions in hydrochloric acid. Figure 1 shows the absorption and luminescence spectra of mesaporphyrin in castor oil* and acid glycerin, and of Zn-mesoporphyrin

*It is interesting to note that several lots of castor oil had to be discarded because the corresponding porphyrin spectra turned out to be intermediate between the "neutral" and "acid" types (this is explained by the presence in the oil of a considerable amount of weak ricinoleic acid).

in castor oil. Figure 2 shows the absorption and luminescence spectra of tetraphenylporphin and its Mg-derivative. In all cases, the luminescence spectra have two

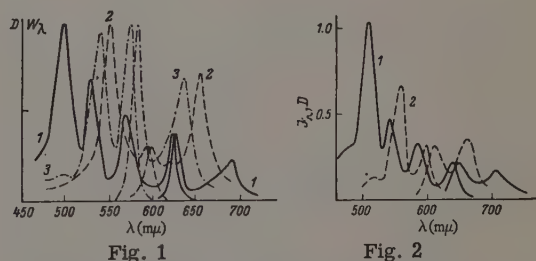


Fig. 1. Absorption and emission spectra. Curve 1—dimethyl ester of mesoporphyrin IX in castor oil; curve 2—in glycerin saturated with HCl; curve 3—Zn-mesoporphyrin in castor oil.

Fig. 2. Absorption and fluorescence spectra. Curve 1—tetraphenylporphin; curve 2—Mg-tetraphenylporphin in isobutyl alcohol.

bands and exhibit mirror symmetry with respect to the two bands in the absorption spectrum.

The dependence of the degree of the fluorescence polarization on viscosity and temperature for several compounds is given in Fig. 3. As the diagram shows, the experimental points give good straight lines when plotted in terms of $1/P$ and T/η , in agreement with the Levshin-Perrin⁵ expression. The lines obtained can be divided into three groups. In the first group, the intercepts of the lines with the ordinate axis (corresponding to the inverses of the intrinsic polarization values) are greater than 7; in the second group they are somewhat below 7, and in the third they are approximately 2.5. The first group includes the metal derivatives of tetraphenylporphyrin, tetrazaporphyrin, and of phthalocyanin; the second—the porphyrins in acid medium and Zn-mesoporphyrin, and the third—the porphyrins in neutral medium and chlorophyll. The difference in the values of the intrinsic fluorescence polarization is apparently due to the different structural symmetries of the π -electron systems of these compounds. The experimental values of the intrinsic fluorescence polarization of the porphyrins and related compounds are summarized in the table.

The compounds investigated were also studied with respect to their polarization spectra. It was found that a decrease of the intrinsic polarization is accompanied by a flattening out of the polarization spectrum. For all compounds in the first and second groups, the degree of polarization is almost independent of the wavelength of the exciting light. Figure 4 depicts the polarization spectrum of protoporphyrin in acid glycerin. Curve 1 represents the degree of polarization of the first fluorescence band (i.e., under the same conditions as in measurements of the intrinsic polarization); curve 2 represents measurements of the second fluorescence band.

DISCUSSION OF RESULTS

It can be seen from the table that limiting value of the degree of polarization of the fluorescence of the magnesium and zinc derivatives of tetraphenylporphyrin (13%) and Mg-azaporphyrin does not exceed the theoretical value for symmetry higher than third order. The data

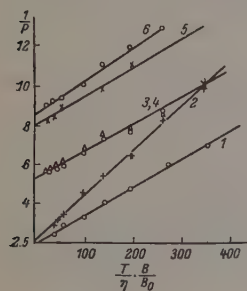


Fig. 3

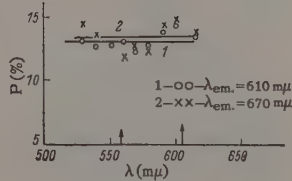


Fig. 4

Fig. 3. Dependence of $1/P$ on $(T/\eta) \cdot (B/B_0)$ for chlorophyll-a (curve 1); tetraphenylporphyrin (curve 2); Zn-mesoporphyrin (curve 3); mesoporphyrin in glycerin saturated with HCl (curve 4); Zn-tetraphenyl porphyrin (curve 5); and phthalocyanin Mg (curve 6) in castor oil. Fig. 4. Polarization spectra for two fluorescence bands of protoporphyrin 1X in glycerin saturated with HCl.

Substance	Solvent	P_0 (%)
Tetraphenylporphyrin	Castor oil	40
Tetrazaporphyrin	Castor oil	40
Mg-tetraphenylporphyrin	Castor oil	13
Zn-tetraphenylporphyrin	Castor oil	13
Mg-tetrazaporphyrin	Castor oil	13
Mesoporphyrin	Castor oil	38
Mesoporphyrin	Glycerin - HCl	18
Zn-mesoporphyrin	Castor oil	17
Protoporphyrin	Castor oil	37
Protoporphyrin	Glycerin - HCl	18
Phenophytin-a*	Castor oil	42
Chlorophyll-a*	Castor oil	42
Protopheophytin**	Castor oil	40
Protochlorophyll	Castor oil	40
Mg-phthalocyanin	Castor oil	13

*Results taken from ref. 11.

**The relative error of measurements may exceed 10%. This is due to the exceedingly low intensity of the long-wavelength absorption band and the low fluorescence yield of protopheophytin.

given in the table and in Fig. 4, along with the structural formula, indicate that these molecules belong to the point symmetry group D_{4h} . This high symmetry indicates the complete equivalence of the pyrrole rings and, therefore, of all four central nitrogen atoms. The metallic atom in the center of the molecule is linked with the nitrogen atom by four identical bonds. All of the symmetrically disposed chemical bonds are also equivalent.

It should be mentioned that the central location of the metal atom in the metalloporphyrin molecule, which had been established on the basis of general chemical considerations, also follows clearly from our measurements.

This high degree of symmetry is undoubtedly due to conjugation. In the metalloporphyrin molecule, the π -electrons must be considered completely delocalized, as in benzene. However, the influence of conjugation in the cases investigated is more complex than in benzene, because the unshared electron pairs of the nitrogen atoms can participate in the conjugated systems.

It must be mentioned that the theoretical value of the degree of polarization ($1/7$) is obtained when the absorption and emission oscillators are located in the plane of the molecule.¹ In highly symmetrical molecules in which the absorption and emission oscillators are perpendicular to the molecular plane, the theoretical value of P_0 is $1/2$; for the totality of a set of "spherical" oscillators, P_0 is zero.

Thus it follows directly from the present results that the long-wavelength absorption oscillator and the corresponding emission oscillator are located in the molecular plane,* and that this is a π - π transition. In-

*Goedheer¹² came to the same conclusion by studying the dichroism of chlorophyll films.

deed, if the transition were of the n - π type, it would be polarized perpendicular to the molecular plane, because the π -electron orbits are antisymmetrical with respect to reflection at the plane of the molecule, whereas the orbits of the unshared electron pairs are symmetrical with respect to this symmetry operation. The fact that the experimental values are close to $1/7$ indicates the complete equivalence of the oscillators located in the molecular plane, and the absence of any component along the z -axis. Quantum-mechanically, this means that the electronic states participating in the long-wavelength transition are doubly degenerate.

The intrinsic polarization in mesoporphyrin and protoporphyrin in an acid medium is also very low (18%), although it exceeds $1/7$. Practically the same value was obtained for Zn-mesoporphyrin (17%). These data indicate that the deviation from the theoretical value for these substances is due to the presence of the side chains, and that the D_{4h} symmetry must be ascribed to the conjugated system of doubly charged ions of the porphyrin and metalloporphyrin molecules. Thus, when two additional protons are introduced into the center of the molecule, a process takes place which is similar to that which occurs when a metal is introduced: the four nitrogen atoms become completely equivalent, and the density of the electronic cloud becomes uniform. Furthermore, the possession of the point symmetry D_{4h} means that the four central protons are located in the molecular plane. Concerning the metalloporphyrins, one can confidently state that even with asymmetrically located side substituents, the metal atom is linked with the central nitrogen atoms by four equivalent bonds.

The low intrinsic polarization values obtained for molecules which are, strictly speaking, asymmetrical, show that in conjugated systems where the absorption and emission of light is due to π -electrons, the decisive influence on the optical properties of the molecules is exercised by the symmetry of the conjugated linkage system, not by the molecular configuration as a whole. However, one cannot neglect the influence of the side chains. The deviation from $1/7$ is larger than the experimental error, and, therefore, there is only an approximate symmetry of the fourth order.

A high intrinsic polarization value (37 to 40%) was obtained for neutral molecules of the porphyrins, which suggests a lower symmetry. By considering the structural formula, one can say that the conjugated system of the neutral porphyrin molecule has the symmetry D_{2h} . The symmetry C_{2v} (adjacent location of the hydrogen atoms in the center of the molecule) would also be possible. However, the assumption of C_{2v} symmetry does not agree with Mason's¹³ studies of the infrared spectra of the porphyrins and N-deuterated porphyrins. Only three frequencies corresponding to the vibration of the N—H bonds are detectable in the spectra, which is correct for D_{2h} symmetry; for C_{2v} symmetry, one would expect five frequencies in the infrared.

The same paper assumes the existence of an intramolecular hydrogen bond in the porphyrins. The porphyrin molecule may have the point symmetry D_{2h} not only if the hydrogen atoms are bonded to the opposite nitrogen atoms (the symmetry axes go through the nitrogen atoms), but also if the hydrogen atoms are bonded to the nitrogen atoms in pairs by the N—H...N linkage (the symmetry axes go through the methine bridges, and the pyrrole rings remain equivalent as they are in the doubly charged ion). In this case, unfortunately, it is not possible to conclude that the pyrrole rings are equivalent on the basis of the polarization data. However, from general considerations, the validity of the intramolecular hydrogen bond hypothesis (first suggested by Robertson¹⁴) is doubtful. The main argument of the supporters of this hypothesis—the considerable frequency shift of the N—H valency vibration as compared with pyrrole—is by no means conclusive. It is much more probable that this change is connected with a substantial change in the state of the nitrogen atom due to the influence of conjugation. The second fact—some elongation of the phthalocyanin molecule revealed by x-ray diffraction¹⁴—also does not

prove anything, inasmuch as the oppositely located protons naturally repel each other, and this easily explains the elongation without the assumption of hydrogen bonds. Opposing this assumption are the stereochemical considerations, which do not favor the formation of intramolecular hydrogen bonds.¹⁵ Furthermore, the spectra of N-methyl porphyrins differ very little from the spectra of the normal porphyrins,¹⁶ whereas the CH_3 group cannot occupy a position between two nitrogen atoms.

The following structure seems the most plausible for porphyrin molecules: The hydrogen atoms are bound by covalent links with two nitrogen atoms which are not equivalent to the other two (tertiary) nitrogen atoms. Because of this, the equivalence of the pyrrole rings is also destroyed, and the conjugated system belongs to the point symmetry group D_{2h} .

It is possible, in principle, that the protons in the center of the porphyrin molecule are capable of shifting from one nitrogen atom to another. This question was discussed by Erdman and Corvin,¹⁶ who concluded that the protons have fixed positions, at least for a period which is longer than the duration of the excited state. Since their reasoning, which is based on the similarity of the spectra of etioporphyrin and of N-methyl etioporphyrin, has been criticized,¹⁷ it is proper to note that the results of polarization measurements completely confirm their conclusion. Indeed, if protons had time to change their position while excited, the oscillator would change its orientation and the fluorescence would be strongly depolarized. Of course, it is more probable that the protons do not change their positions at all. This by no means contradicts the above statement, which is more conservative, but perfectly correct.

In the case of chlorophyll, the most important of all tetrapyrrole pigments, the intrinsic polarization is high and does not differ from that of pheophytin, in spite of the presence of a metal atom in the center of the molecule. This can be easily explained by the fact that because of hydrogenation of one of the pyrrole rings, the symmetry of the conjugated system is greatly distorted, and the introduction of the metal does not enhance the molecular symmetry. By analogy with the porphyrins, one can confidently state that the Mg—N bonds are also equal in the case of chlorophyll, and that the three non-hydrogenated pyrrole rings are equivalent. This raises doubts about the statements found in the literature concerning the existence of chlorophyll isomers differing in the position of Mg—N bonds.¹⁸ It should be noted that there is no generally accepted point of view about the nature of Mg—N bonds in chlorophyll, and one can find several different representations of the center of the chlorophyll molecule.

The structural formula of porphin (I) contains two double bonds, (3—4) and (7—8), which do not enter into the conjugated system according to the formal rule of alternation of single and double bonds. On the other hand, it is clear that the wave functions of the π -electrons of these bonds must overlap with the wave functions of the π -electrons of the conjugated system. As a compromise, the concept of "semi-isolated" double bonds was introduced. The conclusions drawn concerning the symmetry of the porphyrin molecules show that if there is some meaning in the conception of the "semi-isolated" double bonds in the molecules of the porphyrins, then there are also no differences in the side bonds in the metalloporphyrin molecules or the porphyrin ions. One cannot draw such conclusions with certainty concerning the metal

porphyrins. However, the experimental results in general indicate that the three side bonds are also equivalent in this case.

Protochlorophyll, which is now being intensively studied by biologists and biochemists, was investigated by the polarization method. The absorption and luminescence spectra of this compound are given in Fig. 5. The high intrinsic polarization value shows that the presence of the isopentane ring brings about a considerable distortion of the symmetry of the conjugated system.

It must be mentioned that doubt has been expressed by Rabinovich about the (accepted) structure of protochlorophyll.¹⁹ Rabinovich argued that the most intense red band (approx. 620 $m\mu$) in the visible spectrum of protochlorophyll, and the spectrum itself, are similar to those of chlorin. Furthermore, Krasnovskii has found that the behavior of protochlorophyll in photochemical reactions is similar to that of chlorophyll, and not to that of the porphyrins.²⁰ On the other hand, one can argue that the spectrum of the protochlorophyll is similar to those of other metal porphyrins (the intensity of the Soret is more than 10 times greater than the intensity of the red band, and this does not occur in chlorins), and the spectrum of the protopheophytin is typical for the porphyrins which have an isopentane ring. From our point of view, both the high degree of polarization and the above-mentioned anomaly in protochlorophyll can be explained by the asymmetry of the conjugated system due to the isopentane ring, according to the structural formula accepted at present. It is not impossible that this ring is a part of the general system of conjugated bonds, in spite of its lack of alternating single and double bonds (σ - π conjugation).

The intrinsic polarizations of Mg-phthalocyanin and Mg-tetrazaporphin were found to be less than 1/7, which makes it possible to ascribe D_{4h} symmetry to these molecules also. All conclusions concerning the symmetry of the structure of the metal derivatives of tetraphenylporphyrin are also valid in this case.

Polarization measurements show that the introduction of four nitrogen atoms in place of the CH groups of the methine bridges, does not change the symmetry properties of the molecule in any way. It is interesting to note that the spectrum does change greatly (Fig. 6): the first and the third absorption bands become strong, and the second and the fourth bands become weak; the first absorption band of the metal derivatives becomes very strong. Mg-phthalocyanin, whose spectrum is similar to that of chlorophyll, has a particularly strong long-wavelength absorption band. The results obtained show that the intense red band in chlorophyll is connected with the destruction of symmetry, and that the great intensity of this band in Mg-phthalocyanin is due to the aza-substitution, which does not destroy the D_{4h} symmetry. This means that Mg-phthalocyanin is not a direct analogue of chlorophyll, as is usually thought.

Unfortunately, we were unable to measure the degree of polarization of the fluorescence of free phthalocyanin. However, it is quite reasonable to ascribe D_{2h} symmetry to this molecule by analogy with the porphyrins, and also on the basis of the previously mentioned x-ray diffraction data.¹⁴ Such data are available for Ni-phthalocyanin and Pt-phthalocyanin.²¹ In the case of Ni-phthalocyanin it was found that the distances between the opposite nitrogen atoms in the two mutually perpendicular directions differ by 0.06 Å. This result appears strange because this difference is zero (point symmetry

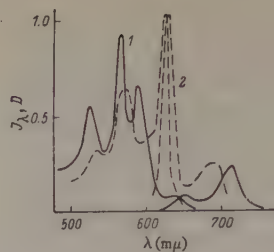


Fig. 5

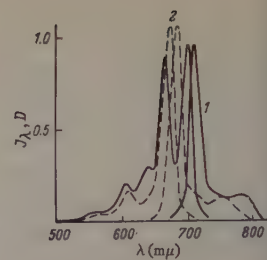


Fig. 6

Fig. 5. Absorption and fluorescence spectra of protopheophytin (curve 1) and of protochlorophyll (curve 2) in isobutyl alcohol. Fig. 6. Absorption and fluorescence spectra of phthalocyanin (curve 1) in quinoline, and of Mg-phthalocyanin (curve 2) in isobutyl alcohol.

D_{4h}) in Pt-phthalocyanin; for Mg-phthalocyanin the symmetry D_{4h} follows from the value of the intrinsic polarization, and for nickel, dsp_2 hybridization is characteristic, and this would lead to a more symmetrical structure. The assignment of D_{2h} symmetry to the free phthalocyanin molecule finds additional support in the value obtained for the intrinsic polarization of the fluorescence of tetrazaporphin (40%).

The degree of polarization in the second fluorescence band also does not depend on the wavelength, and is close to 1/7. As for the Soret band, the degree of polarization upon excitation in this band is close to 1/7 even for D_{2h} symmetry. From this fact, and on the basis of the curves (Figs. 1 and 3), one can conclude that each absorption and emission band of metal-porphyrins and porphyrins in an acid medium corresponds to a two-dimensional oscillator.

In conclusion, let us consider the connection between the symmetry and the molecular spectra of the porphyrins. As early as 1942, Pruckner, while studying the intensity of the long-wavelength absorption band of the azaporphyrins as a function of the number and position of the nitrogen atoms introduced, concluded that the intensity of the bands increases with increasing molecular symmetry. From this finding, Pruckner proceeded to the quite erroneous conclusion that the structure of the chlorins is more symmetrical than that of the porphyrins.²² Erdman and Corvin's assumption (the correctness of which is now evident), that the two-band spectrum corresponds to D_{4h} symmetry and the four-band spectrum to D_{2h} , was used later by Platt²³ and by Blumenfeld²⁴ for suggesting qualitative interpretations of the spectra of the porphyrins (it should be noted that these two interpretations are radically different). Measurements of intrinsic polarization, of course, cannot decide on the correctness of these interpretations. There is no doubt, however, that the increase in the symmetry of the porphyrin molecule from the second to the fourth order is accompanied by a decrease in the number of bands in the visible region of the spectrum.

Thus, the result obtained for Mg-phthalocyanin fits naturally into the general experimental picture.

In conclusion, the writers express their sincere gratitude to M. A. El'yashevich and B. I. Stepanov for valuable discussions during the present investigation and to M. G. Gurevich for help in preparing the samples.

REFERENCES

1. P. P. Feofilov, *Doklady Akad. Nauk SSSR*, **57**, 343 (1947).
2. A. Jablonski, *Z. Physik* **96**, 236 (1935).
3. M. Grinstein and C. J. Watson, *J. Biol. Chem.* **167**, 515 (1947);
R. H. Ball, G. D. Dorough, and M. Calvin, *J. Am. Chem. Soc.* **68**, 2278 (1946).
4. M. Grinstein and C. J. Watson, *J. Biol. Chem.* **147**, 671 (1943).
5. V. L. Levshin, "Fotoluminesentsiya zhidkikh i tverdykh veshchestv" (Photoluminescence of Liquid and Solid Substances). Moscow-Leningrad, 1951.
6. J. W. Weigl, *J. Mol. Spectroscopy* **1**, 133 (1957).
7. G. P. Gurinovich, *Trudy Inst. Fiz. i Mat. Akad. Nauk Belorus.SSR* **3**, 111 (1959).
8. G. P. Gurinovich and A. N. Sevchenko, *Izvest. Akad. Nauk SSSR, Ser. Fiz.* **22**, 1407 (1958).
9. A. Stern and H. Wenderlein, *Z. physik. Chem. (Leipzig)* **170A**, 337 (1934); **174A**, 81 (1935);
A. Stern and M. Dezelic, *Z. physik. Chem. (Leipzig)* **180A**, 131 (1937).
10. G. D. Dorough, J. R. Miller, and F. M. Huennekens, *J. Am. Chem. Soc.* **73**, 4315 (1951).
11. G. P. Gurinovich, I. N. Ermolenko, A. N. Sevchenko, and K. N. Solov'ev, *Opt. i Spekt.* **3**, 237 (1957).
12. J. C. Coedheer, *Nature*, **176**, 928 (1955).
13. S. F. Mason, *J. Chem. Soc.* 976 (1958).
14. J. M. Robertson, *J. Chem. Soc.* 1195 (1936).
15. J. Donohue, *J. Phys. Chem.* **56**, 502 (1952).
16. J. G. Erdman and A. H. Corvin, *J. Am. Chem. Soc.* **68**, 1885 (1946).
17. S. Aronoff, *Chem. Revs.* **47**, 175 (1950).
18. S. Freed, K. M. Sancier, and A. H. Sporer, *J. Am. Chem. Soc.* **76**, 6006 (1954).
19. E. Rabinovich, "Fotosintez" (Photosynthesis), Vol. 2. Moscow, 1952.
20. L. A. Krasnovskii, *Doklady Akad. Nauk SSSR* **60**, 421 (1948).
21. J. M. Robertson and J. Woodward, *J. Chem. Soc.* 219 (1937); *Ibid.* 36 (1940).
22. F. Pruckner, *Z. physik. Chem. (Leipzig)* **190A**, 101 (1942).
23. J. R. Platt, *Radiation Biol.* **3**, 71 (1956).
24. L. A. Blyumenfel'd, "Gemoglobin i obratimoe prisoedinenie kisloroda" (Hemoglobin and Reversible Association of Oxygen). Moscow, 1957.

STUDY OF THE NATURE OF THE BONDING FORCES OF ASSOCIATED DYE MOLECULES IN CONCENTRATED SOLUTIONS

L. V. Levshin and V. K. Gorshkov (pp. 759-766)

Received 15 June 1960

The concentration and temperature dependences of the absorption spectra of the dyes rhodamine C, Magdala red, and crystal violet have been studied. For the first two dyes, the bonding energy of the associated molecules has been determined; for the third, the formation in concentrated aqueous solutions not only of dimers, but also of higher complexes has been established. On the basis of the bonding energy values obtained and the structure of the molecules studied, the conclusion is drawn that the formation of the complexes is fundamentally brought about by the formation of a hydrogen bond.

INTRODUCTION

The formation of associated dye molecules in concentrated aqueous solutions is at present a firmly established fact. At the same time, the question of the nature of the forces which bring about association of charged particles of the same sign has not been finally elucidated. According to the opinion of some authors, the association is brought about by forces of van der Waals type;^{1,2} others consider that the hydrogen bond is responsible for the formation of the complexes.^{3,4} For the solution of this basic question, it is very important to know the values of the bonding energy of the associated molecules, which differ substantially for different types of interaction. Thus for van der Waals interaction this energy is of the order of 1 kcal/mole, while it is ~10 kcal/mole when a hydrogen bond is formed. However, it should be noted that the quantities mentioned have been determined only in very few cases.^{1,4-7}

In the present work, the authors have endeavored to enlarge the existing scanty data on the bonding energy values for associated dye molecules, and to give an answer to the question of the nature of the forces responsible

for their formation. Three dyes which associate well in concentrated aqueous solutions^{8,9}—rhodamine C, Magdala red, and crystal violet—were chosen as objects of study.

In our work, we studied the concentration and temperature dependence of the absorption spectra of aqueous solutions of these substances. The data obtained enable us to determine the magnitude of the bonding energy of the complexes.⁵ Actually, in the case of a binary mixture, the following relationship is valid¹⁰:

$$\frac{X^2}{1-X} = \frac{D}{C\sqrt{T}} e^{-\frac{U}{kT}}, \quad (1)$$

where X is the fraction of monomer at a given solution concentration C, U is the association energy, D is the equilibrium constant, and T is the absolute temperature. Taking logarithms in expression (1), we obtain:

$$\log \frac{X^2}{1-X} + \log C + \frac{1}{2} \log T - \log D = -\frac{U}{k} \frac{1}{T} \log e. \quad (2)$$

It can be seen from expression (2) that there exists a linear dependence between the quantities $\log\{[X^2/(1-X)]C\sqrt{T}\}$ and $1/T$. Plotting the quantity $\log\{[X^2/(1-X)]C\sqrt{T}\}$ against $1/T$, we obtain a straight line with a negative slope.

X)] $C\sqrt{T}$ along the ordinate axis and $1/T$ along the abscissa axis, we obtain a straight line, the tangent of whose angle with the horizontal axis equals

$$\tan \varphi = -\frac{U}{k} \log e, \quad (3)$$

from which the magnitude of the bonding energy of the associated molecules, U , can be determined.

It can be seen from Eq. (2) that, in order to construct the appropriate straight line, it is necessary to know the fraction of monomer X in the solution at a given temperature T . The value of X may be determined by using the expression

$$X = \frac{\alpha - \alpha_D}{\alpha_M - \alpha_D}, \quad (4)$$

where α_M , α_D , and α are the absorption coefficients at a fixed wavelength λ for monomers, dimers, and the solution under study, respectively.^{8,11,12} The value of α_M is determined from the absorption spectrum of a highly diluted solution ($C \sim 1 \times 10^{-6}$ gm/ml); α is taken from the absorption spectra measured at different temperatures and α_D is computed from concentration experiments by the method described in refs. 8, 11, and 12.

RESULTS OF THE MEASUREMENTS

In Fig. 1 is presented the concentration dependence of the absorption spectra of aqueous solutions of rhodamine C. It can be seen from the figure that, as the concentration increases, the intensity of the long-wavelength monomer maximum ($\lambda_{\max} = 555$ m μ) falls off rapidly, and at the same time the short-wavelength maximum belonging to the associated molecules ($\lambda_{\max} = 525$ m μ) grows, all the spectra intersecting in an isosbestic point ($\lambda = 535$ m μ). The latter fact is evidence that the solutions under investigation are binary mixtures of monomers and associated molecules of rhodamine C.*

*It has been established for the dyes investigated that changes in the pH value cannot be responsible for the deformation of their absorption spectra which takes place as the solution concentration is increased.⁹

The absorption spectrum remains unchanged at concentrations less than $\sim 1 \times 10^{-6}$ gm/ml, which allows us to ascribe it to monomers (curve 1). The absorption spectrum of the complexes, obtained on the basis of the calculation described in refs. 8, 11, and 12, is also presented in Fig. 1 (curve 8).

An increase in temperature leads to an increase in the vibrational energy of the associated molecules and is accompanied by their progressive breakdown. Therefore, when a concentrated solution is heated, the intensity of the short-wavelength maximum must diminish and that of the long-wavelength one increase; i.e., at sufficiently high temperatures the monomer absorption spectrum must be restored. As an example, the temperature dependence of the absorption spectrum of a solution of rhodamine C in water ($C = 2 \times 10^{-3}$ gm/ml) is presented in Fig. 2. It can be seen from the figure that, as the temperature is raised, disappearance of the short-wavelength maximum and restoration of the long-wavelength one actually take place.

It should be noted, however, that complete restoration of the monomer maximum is not observed even when the short-wavelength maximum has already completely

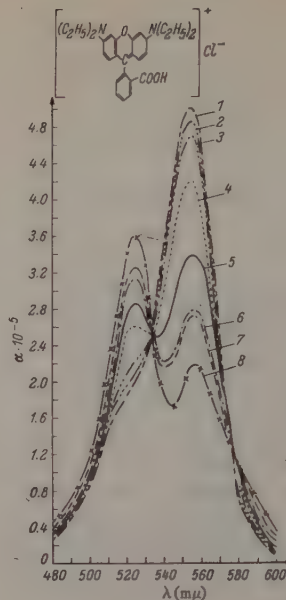


Fig. 1

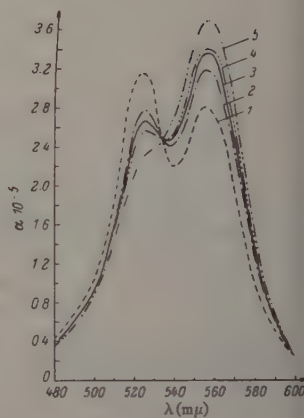


Fig. 2

Fig. 1. Concentration dependence of the absorption spectrum of an aqueous solution of rhodamine C. Concentration (gm/ml): curve 1— 1×10^{-6} ; curve 2— 1×10^{-5} ; curve 3— 2×10^{-5} ; curve 4— 1×10^{-4} ; curve 5— 4×10^{-4} ; curve 6— 2×10^{-3} ; curve 7— 3×10^{-3} ; curve 8—absorption spectrum of the complexes.

Fig. 2. Temperature dependence of the absorption spectrum of an aqueous solution of rhodamine C (concentration 2×10^{-3} gm/ml). Temperature ($^{\circ}\text{C}$): curve 1—18; curve 2—50; curve 3—60; curve 4—70; curve 5—95.

disappeared. This is explained by the fact that, as the temperature is raised, a change takes place not only in the short-wavelength absorption maximum but also in the long-wavelength one. One can satisfy oneself of this by heating highly diluted solutions. This phenomenon has previously been observed with certain other compounds also.^{1,13} As a rule, heating leads to a general fall in the intensity of the monomer absorption band, thereby not permitting complete restoration of the absorption spectrum pertaining to the unheated dilute solution.*

*The change in the absorbing power of dilute solutions with temperature has a rather complex character and depends strongly on the concentration of the solution. Its description and interpretation will be given in a following communication.

The absorption spectra of aqueous solutions of the dye Magdala red behave in an analogous manner.⁸ As the concentration increases, the intensity of the long-wavelength monomer maximum ($\lambda_{\max} = 555$ m μ) diminishes and that of the short-wavelength maximum ($\lambda_{\max} = 525$ m μ) increases, all the spectra intersecting at a point where $\lambda = 535$ m μ . Heating of concentrated solutions leads to a breakdown of the associated molecules (Fig. 3).

A different picture may be observed in the case of the absorption spectra of aqueous solutions of the dye crystal violet (Fig. 4). As the concentration increases, the form of the monomer spectrum (curve 1) at first re-

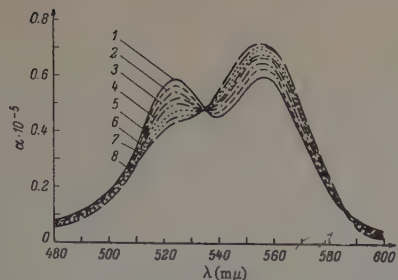


Fig. 3. Temperature dependence of the absorption spectrum of an aqueous solution of Magdala red (concentration 5×10^{-3} gm/ml). Temperature ($^{\circ}\text{C}$): curve 1—20; curve 2—30; curve 3—40; curve 4—50; curve 5—60; curve 6—70; curve 7—80; curve 8—90.

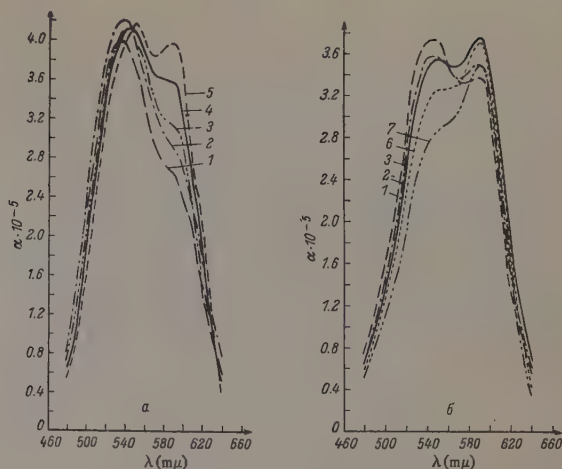


Fig. 5. Temperature dependence of the absorption spectra of aqueous solutions of crystal violet of different concentrations. Concentration (gm/ml): a— 2×10^{-3} ; b— 4×10^{-4} . Temperature ($^{\circ}\text{C}$): curve 1—22; curve 2—35; curve 3—50; curve 4—70; curve 5—90; curve 6—65; curve 7—80.

remains substantially unchanged—a marked increase in absorbing power over the whole spectrum is all that takes place (curve 2). Then the short-wavelength part of the absorption spectrum begins gradually to grow in intensity. This growth is accompanied by a decrease in the height of the monomer maximum ($\lambda_{\text{max}} = 585 \text{ m}\mu$). The intensity of the short-wavelength maximum ($\lambda_{\text{max}} = 540 \text{ m}\mu$) reaches a maximum value at $C = 1 \times 10^{-3}$ gm/ml (curve 5). On a further increase in the concentration (curve 6), its height diminishes somewhat. Apparently, this takes place on account of a further decrease in the intensity of the long-wavelength monomer part of the absorption spectrum, which overlaps the absorption spectrum of the complexes.

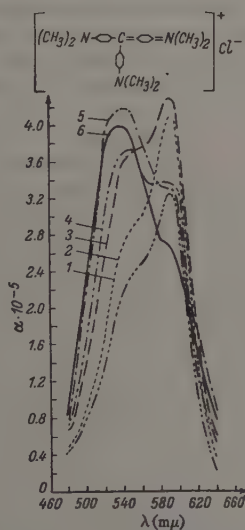


Fig. 4. Concentration dependence of the absorption spectrum of an aqueous solution of crystal violet. Concentration (gm/ml): curve 1— 1×10^{-6} ; curve 2— 1×10^{-5} ; curve 3— 1×10^{-4} ; curve 4— 4×10^{-4} ; curve 5— 1×10^{-3} ; curve 6— 2×10^{-3} .

It should be noted that the curves presented in Fig. 5 refute the assertion contained in ref. 5 concerning the presence of a common point of intersection in the absorption spectra of aqueous crystal violet solutions of different concentrations. The complex character of the concentration dependence of the absorption spectra and the absence of an isosbestic point compel us to assume

that, along with monomers, there exist associated molecules of varying complexity in aqueous solutions of crystal violet. Then each type of complex will have its own absorption spectrum, each of which overlaps the others.

The temperature dependence of the absorption spectra of a concentrated solution of crystal violet ($C = 2 \times 10^{-3}$ gm/ml) is presented in Fig. 5a. It can be seen from the figure that on heating one observes at first, at the same time as the increase in the intensity of the monomer maximum (curve 2), a certain increase in the height of the absorption maximum of the complexes ($\lambda_{\text{max}} = 540 \text{ m}\mu$). On further elevation of the temperature, the short-wavelength maximum changes very little, while the long-wavelength maximum increases markedly in intensity. The process of disappearance of the short-wavelength maximum on heating may also be followed at lower solution concentrations. The temperature dependence of the absorption spectrum of an aqueous solution of crystal violet at $C = 4 \times 10^{-4}$ gm/ml is presented in Fig. 5b. It can be seen from the figure that the fall in intensity of the short-wavelength maximum is at first accompanied by a corresponding increase in the long-wavelength maximum (curves 2 and 3). However, at a higher temperature no such compensation takes place; i.e., a fall in the intensity of both maxima is observed (curves 4 and 5). It should be noted that the intensity of the long-wavelength maximum begins to diminish without having reached the values which might have been expected on the basis of the curves presented in Fig. 4. This is apparently also explained by the presence of the temperature effect of which we spoke above in describing the temperature dependence of the absorption spectra of rhodamine C.

Thus, when concentrated solutions of crystal violet are heated, the course of the changes of its absorption spectra with concentration is qualitatively repeated in the reverse direction. This gives evidence first of all that the concentration effects in the absorption spectra of crystal violet are brought about by the association of its molecules. These complexes are quite stable: in the solutions studied, we did not succeed in breaking them down completely even on heating to $t \sim 100^{\circ}\text{C}$.

DISCUSSION OF RESULTS

The concentration and temperature dependences obtained for the absorption spectra of solutions of rhodamine C and Magdala red permit us to determine the magnitudes of the bonding energy of their associated molecules. For this, the appropriate straight lines were set up by the method indicated above for four rhodamine C solutions of different concentrations and three Magdala red solutions. As an example, two of them are presented in Fig. 6 (curve 1 for rhodamine C and curve 2 for Magdala red). The values determined from these graphs for the bonding energy of the complexes are presented in Table 1.

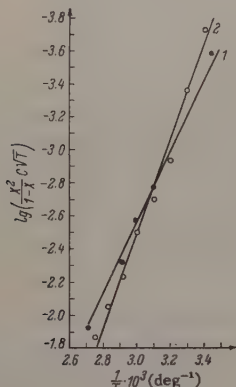


Fig. 6. Dependence of $\lg\{[X^2/(1-X)]C\sqrt{T}\}$ on $1/T$. Curve 1—rhodamine C (concentration 2×10^{-3} gm/ml); curve 2—Magdala red ($C = 5 \times 10^{-3}$ gm/ml).

It can be seen from the table that the bonding energy value for the complexes of both dyes exceeds 10 kcal/mole, which is a whole order of magnitude larger than the bonding energy value resulting from van der Waals interaction. Consequently, the presence of forces of the latter type is quite insufficient for the formation of associated molecules of the substances studied. On the other hand, the values of U obtained correspond to the known values of hydrogen bond forces. In this connection, the structure of the molecules studied fully allows the possibility of the formation of a hydrogen bond between them. Actually, there are OH and oxygen groups in rhodamine C, and amino groups and nitrogen atoms in the molecules of Magdala red.

Table 1

$C \times 10^{-4}$ (gm/ml)	U (kcal/mole)	
	Rhodamine C	Magdala red
1	9.9	—
4	10.0	—
10	—	11.8
20	10.2	12.5
30	11.2	—
50	—	13.1

The two circumstances cited give a basis for considering that the concentration effects described in the absorption spectra of the dyes studied are brought about by the formation of associated molecules of a single type, joined together by means of a hydrogen bond. At the same time, the question of whether the hydrogen bonds form directly between the dye molecules or whether water

molecules are an intermediate link between them still remains open.

In consequence of the fact that there is no isosbestic point in the absorption spectra of crystal violet, it does not appear possible to compute the bonding energy of its associated molecules by the method described. However, the temperature experiments show that the breakdown of its complexes takes place over approximately the same temperature interval as for rhodamine C and Magdala red. This gives grounds for supposing that the magnitude of the bonding energy of its complexes is of the same order as for the latter two dyes.

It is interesting to note that, in all the cases known to us from the literature, the magnitudes obtained for the bonding energy of associated dye molecules were also considerable. For comparison, these data are presented in Table 2, together with our results.

Table 2

No.	Substance	U (kcal/mole)	Reference
1	Magdala red	$\sim 13^*$	This work
2	Rhodamine C	$\sim 10^*$	This work
3	Rhodamine 6G	$\sim 7^*$	Ref. 4
4	Rhodamine 3B	$\sim 5^*$	Ref. 4
5	Methylene blue	5.4	Ref. 5
6	Acridine orange	8.4	Ref. 6
7	Pseudoisocyanine	13	Ref. 7
8	Thionine	6.8	Ref. 1

*Exact values are not given, since for these substances the value of the bonding energy of the associated molecules depends on the concentration of the solution.

It can be seen from the data presented that the bonding energy of these associated molecules has a value from 5 to 13 kcal/mole; i.e., it markedly exceeds the limiting values possible for it in the case of van der Waals interaction. Together with this, the structure of the molecules of these compounds also allows one to assume the formation of a hydrogen bond between them.

Thus the formation of a hydrogen bond is apparently the basic cause which brings about the formation of associated molecules of these compounds. At the same time it is very probable that, aside from the hydrogen bond, there also exists between them a van der Waals interaction which, however, is not large and plays a subordinate role.

From the data presented in Table 1 it can be seen that the bonding energy of associated molecules of rhodamine C and Magdala red gradually increases as the concentration of the solution increases. To be sure, this increase is not large and lies within the limits of error of the experiment (the accuracy of the determination of $U \approx \pm 15\%$). However, these changes have an entirely regular character for both substances. An analogous phenomenon was found by Baranova and Levshin for aqueous solutions of rhodamine 6G and 3B.⁴ This permits us to assume that a dependence of the quantity U on the concentration of the solution actually does exist. The increase in the value of U in concentrated solutions may be explained by the formation in them not only of dimers, but also of higher complexes, for the breakdown of which (into the dimeric state) additional energy is required.*

*In this case the solution ceases to be binary, and the starting equations lose their force.

At the same time, the number of these complexes must be small, since their presence does not manifest itself in

the absorption spectra (the isosbestic point remains unchanged).

REFERENCES

1. E. Rabinowitch and L. Epstein, *J. Am. Chem. Soc.* **63**, 69 (1941).
2. Th. Förster, *Fluoreszenz organischer Verbindungen*. Göttingen, 1951.
3. S. Sheppard, *Revs. Modern Phys.* **14**, 303 (1942).
4. E. G. Baranova and V. L. Levshin, *Opt. i Spektr.* **10**, 362 (1961), *Optics and Spectroscopy* **10**, 182 (1961).
5. T. P. Kravets, A. L. Pes'kina, and Z. V. Zhidkova, *Izvest. Akad. Nauk SSSR, Ser. Fiz.* **14**, 483 (1950).
6. V. Zanker, *Z. physik. chem.* **B119**, 225 (1952).
7. L. D. Derkacheva, *Izvest. Akad. Nauk SSSR, Ser. Fiz.* **20**, 410 (1956).
8. L. V. Levshin and V. G. Bocharov, *Opt. i Spektr.* **10**, 627 (1961), *Transl. Ed. note: this reference cannot be traced*.
9. L. V. Levshin, "Thermodynamics and the Structure of Solutions," p. 285. *Izd. Akad. Nauk SSSR, Moscow*, 1959.
10. Ya. I. Frenkel', "Statistical Physics," p. 377. *Izd. Akad. Nauk SSSR, Moscow-Leningrad*, 1948.
11. V. L. Levshin and E. G. Baranova, *Opt. i Spektr.* **6**, 55 (1959), *Optics and Spectroscopy* **6**, 31 (1959).
12. V. L. Levshin, E. G. Baranova, L. D. Derkacheva, and L. V. Levshin, "Thermodynamics and the Structure of Solutions," p. 275. *Izd. Akad. Nauk SSSR, Moscow*, 1959.
13. L. V. Levshin, *Zhur. Eksptl. i Teoret. Fiz.* **28**, 201 (1955). *Soviet Phys.-JETP* **1**, 244 (1955).

STUDY OF THE EQUILIBRIA IN NONAQUEOUS SOLUTIONS OF ELECTROLYTES BY MEANS OF ABSORPTION SPECTRA

II. Picric Acid and Sodium Picrate in Acetic Acid, Pyridine, Acetonitrile, and Acetone

N. A. Izmailov and E. L. Gurevich (pp. 767-772)

Received 6 July 1960

The absorption spectra of solutions of picric acid and sodium picrate in acetic acid, pyridine, acetone, and acetonitrile have been studied. The presence of equilibria between the ions and molecules of picric acid in acetone and acetonitrile has been established, and also between the ions and ion pairs of sodium picrate in acetone, acetonitrile, and pyridine. Dissociation constants have been computed for picric acid at a concentration of 1×10^{-3} moles/liter in acetone and acetonitrile.

A preceding communication¹ was devoted to the investigation of the absorption spectra of picric acid and sodium picrate in leveling solvents—water and alcohols. The presence of equilibria between the ions and molecules of picric acid and between the ions and ion pairs of sodium picrate in these solvents was established.

In the present communication, we set forth the results of an investigation of the absorption spectra of picric acid and sodium picrate in solvents with pronounced acidic and basic properties—acetic acid and pyridine (their dielectric constants equal 6.13 and 12.5 respectively)—and also in such differentiating solvents as acetonitrile and acetone (their dielectric constants equal 36.7 and 19.1 respectively).

As in the preceding work, all the absorption spectra were measured using an SF-4 apparatus. The same concentrations of picric acid and sodium picrate as in ref. 1 were chosen for this investigation, namely, 5×10^{-5} , 1×10^{-3} , and 8.8×10^{-3} moles/liter, and correspondingly cells of thickness 1, 0.05, and 0.0057 cm. All substances were carefully purified and dried; the absorption spectra of freshly prepared solutions were studied, and then the long-term stability of the spectra obtained was checked. It was found that picric acid dissociates slowly in acetone (this has also been noted by other authors²). For a more detailed study of this phenomenon, all the picric acid and sodium picrate solutions prepared in acetone were sealed into ampoules. Three ampoules were prepared for each concentration and were opened immedi-

ately before the measurements. The measurements were carried out over a period of 312 days.

Let us turn to a consideration of the data obtained.

In 100% acetic acid, picric acid and sodium picrate possess similar absorption spectra, which correspond to the undissociated acid (Fig. 1). For comparison, the spectral curve of undissociated picric acid in dichloroethane is shown on the graph by a broken line; it is characterized by two maxima in the region of 238 and 340 m μ . This agreement indicates an interaction of so-

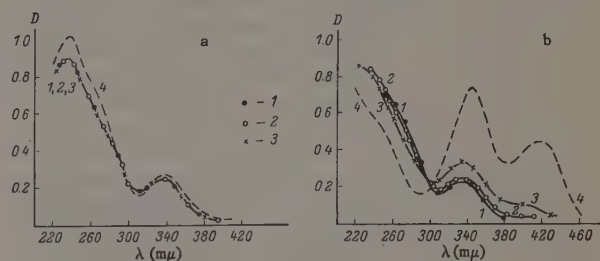


Fig. 1. Absorption spectra of solutions of picric acid (a) and sodium picrate (b) in glacial acetic acid at various concentrations. Concentration (moles/liter): curve 1— 5×10^{-5} ; curve 2— 1×10^{-3} ; curve 3— 8.8×10^{-3} ; curve 4—absorption spectra of the same substances in dichloroethane (a) and dioxane (b).

dium picrate with acetic acid with the formation of picric acid. The proton-donating properties of acetic acid and its low dielectric constant repress the dissociation of picric acid. The spectrum of sodium picrate at a concentration of 8.8×10^{-3} moles/liter differs somewhat from the picric acid spectrum. This indicates that sodium picrate at this concentration is already only partially converted into picric acid and is beginning to show its own properties (cf. the spectrum of the ion pairs of sodium picrate in dioxane—broken line).

The absorption spectra of picric acid and sodium picrate in pyridine also possess a great similarity at all concentrations (Fig. 2). In this case, picric acid enters into an interaction with the solvent with the formation of a salt-like product which absorbs identically with sodium picrate. As the concentration increases, a shift of the spectra toward shorter wavelengths is observed; i.e., in the direction of the spectra of the ion pairs of sodium picrate. At a concentration of 5×10^{-5} moles/liter, picric acid and sodium picrate have one and the same absorption spectrum, which is characterized by a maximum in the region of 382 m μ and is an ion spectrum. For comparison, the spectrum of the ions of picric acid and sodium picrate in water is presented in the same figure (broken line); this is characterized by a maximum in the region of 355–356 m μ . The spectrum of the ions of picric acid and sodium picrate in pyridine is displaced toward longer wavelengths relative to the ion spectrum in water.

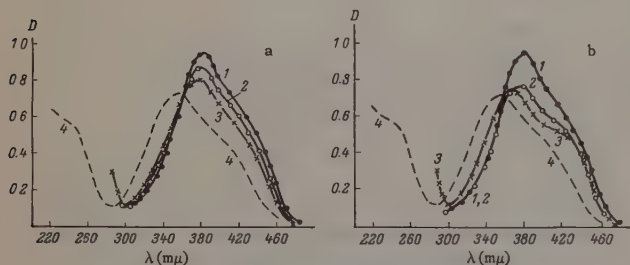


Fig. 2. Absorption spectra of solutions of picric acid (a) and sodium picrate (b) in pyridine at various concentrations. For concentrations (curves 1, 2, 3), see legend to Fig. 1; curve 4—absorption spectra of the same substances in water.

Picric acid in acetonitrile at concentrations of 5×10^{-5} , 1×10^{-3} , and 8.8×10^{-3} moles/liter is characterized by three spectral curves intersecting in a single point (Fig. 3). Picric acid and sodium picrate at a concentration of 5×10^{-5} moles/liter possess completely identical spectra with a maximum in the region of 375 m μ (ion spectra). Picric acid at a concentration of 8.8×10^{-3} has a spectrum similar to the spectrum of undissociated picric acid. The point of intersection of the spectral curves indicates an equilibrium between the ions and molecules of picric acid in acetonitrile. The absorption spectra of sodium picrate in acetonitrile and acetone at concentrations of 5×10^{-5} and 8.8×10^{-3} moles/liter are presented in the same figure. At a concentration of 5×10^{-5} moles/liter, sodium picrate gives the spectrum of the ions, with maxima at 375 m μ in acetonitrile and 378 m μ in acetone. A shift of the spectrum and a displacement of the maximum toward shorter wavelengths, i.e., toward the spectrum of ion pairs, are already observable at a sodium picrate concentration of 8.8×10^{-3} moles/liter.

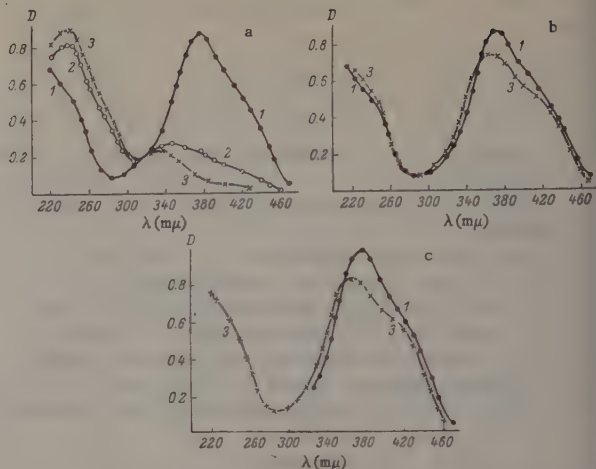


Fig. 3. Absorption spectra of solutions of picric acid in acetonitrile (a) and of sodium picrate in acetone (c) and acetonitrile (b) at various concentrations. For concentrations (curves 1, 2, 3), see legend to Fig. 1.

On addition of sodium perchlorate—a readily soluble salt with a common ion—to solutions of sodium picrate in acetonitrile and acetone, marked band shifts and changes in the character of the spectra are observed (Fig. 4). The spectral curve is then characterized by two maxima (in the regions of 350 and 410 m μ), being the spectrum of the associated ions of sodium picrate (cf. with the spectrum of sodium picrate in dioxane—the broken line in Fig. 1).

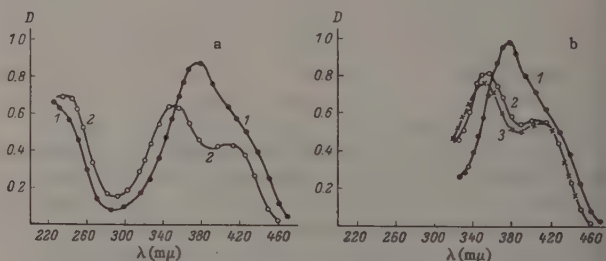


Fig. 4. Absorption spectra of solutions of sodium picrate (concentration 5×10^{-5} moles/liter) in acetonitrile (a) and acetone (b) without additions (curve 1) and with the addition of sodium perchlorate (curves 2, 3). Quantity of NaClO_4 added: (a) curve 2—1.9N; (b) curve 2—1N; curve 3—2.7N.

In acetone, as has already been noted above, the degree of dissociation of picric acid is observed to change with time. It has been established for sodium picrate that the absorption spectra do not change with time. At concentrations of 5×10^{-5} and 1×10^{-3} moles/liter, sodium picrate is fully dissociated at once; the spectral curve (which corresponds to that of the ions) does not change with time. The spectral curve of sodium picrate at a concentration of 8.8×10^{-3} moles/liter is displaced relative to the ion spectrum (Fig. 3) and likewise does not change with time.

An entirely different picture is observed for picric acid, for which a temporal variation in the spectra takes place at all concentrations. In Fig. 5 are presented the spectra of picric acid at a fixed concentration, measured

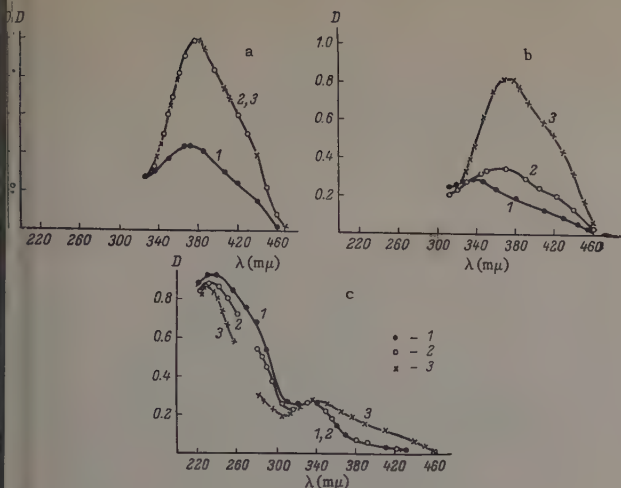


Fig. 5. Absorption spectra of solutions of picric acid in acetone at a fixed concentration, obtained at different times from the moment of preparation of the solutions. Concentration (moles/liter): a— 5×10^{-5} ; b— 1×10^{-3} ; c— 8.8×10^{-3} . Time elapsed from the moment of preparation of the solution: curve 1—16 hr; curve 2—6 days; curve 3—312 days.

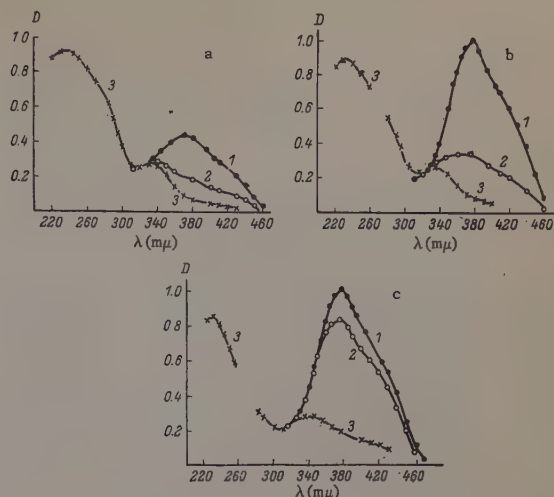


Fig. 6. Absorption spectra of solutions of picric acid in acetone at various concentrations, obtained at different times from the moment of preparation of the solutions. Time elapsed from the moment of preparation of the solutions: a—16 hr; b—6 days; c—312 days. Concentration (moles/liter): curve 1— 5×10^{-5} ; curve 2— 1×10^{-3} ; curve 3— 8.8×10^{-3} .

At different times. At a concentration of 5×10^{-5} moles/liter, the initial curve is close to the spectrum of the molecular form, but after the lapse of 6 days the solution is already characterized by a spectral curve which coincides with the ionic spectrum of sodium picrate in acetone. This is evidence that the picric acid has dissociated completely. The spectra of picric acid at concentrations of 1×10^{-3} and 8.8×10^{-3} moles/liter also change with time, the spectral curves converging to a single point in all the cases presented.

In Fig. 6 the absorption spectrum of the picric acid is presented at various concentrations, measured at different times. The time-dependent variation in the dissociation of the acid can be plainly seen from this figure also. The spectral curves intersect in a single point, which indicates an equilibrium between ions and molecules.

Freshly distilled acetone at a layer thickness of 1 cm absorbs light down to 320 mμ. However, in thinner layers (for example, at a thickness of 0.0057 cm) acetone is optically transparent over the whole wavelength region investigated, and the spectra of picric acid and sodium picrate at a concentration of 8.8×10^{-3} moles/liter may be obtained in their entirety. On long standing of the ampoules containing the solutions, acetone, even in thin layers, begins to absorb in the interval from 258 to 282 mμ, which accounts for the breaks in the spectral curves of picric acid in this region at a concentration of 8.8×10^{-3} moles/liter (Figs. 5 and 6).

Thus in acetone and in acetonitrile (just as in alcohols) an equilibrium is established between the ions and the molecules of picric acid, and also between the ions and ion pairs of sodium picrate.

According to our calculations, the dissociation constant of picric acid at a concentration of 1×10^{-3} moles/liter in acetonitrile equals 4.57×10^{-5} ($pK = 4.34$).

According to the data of ref. 3, the dissociation constant of picric acid in acetonitrile equals 1×10^{-5} ($pK = 5$). This value was determined using the indicator method, the authors themselves indicate that it is not very exact.

The dissociation of picric acid in acetone changes with time. Therefore, the apparent dissociation constants of picric acid at a concentration of 1×10^{-3} moles/liter calculated after 16 hr, 6 days, and 312 days from the moment of preparation of the solutions equal 1.86×10^{-5} , 1.12×10^{-4} , and 3.87×10^{-3} , respectively.

The dissociation constant of picric acid in acetone calculated from the electrical conductivity data of Moore and Johns⁴ equals 1.38×10^{-4} . We consider the value of this constant to be very unreliable, since picric acid dissociates slowly and it is not known whether a stable value of the dissociation constant was attained. Later French and Roe⁵ showed that the electrical conductivity of solutions of picric acid in acetone changes with time (they studied the conductivity of picric acid solutions from 4×10^{-5} to 1×10^{-1} N in acetone and acetonitrile). These authors⁵ assumed the formation of ion triplets of the type $(Pk-H-Pk)^-$.

REFERENCES

1. N. A. Izmailov and E. L. Gurevich, *Opt. i Spekr.* 10, 19 (1961), *Optics and Spectroscopy* 10, 9 (1961).
2. C. M. French and J. G. Roe, *Trans. Faraday Soc.* 49, 791 (1953).
3. M. Kilpatrick and M. Kilpatrick, *Chem. Revs.* 13, 131 (1933).
4. F. J. Moore and J. B. Johns, *J. Am. Chem. Soc.* 63, 3336 (1941).
5. C. M. French and J. G. Roe, *Trans. Faraday Soc.* 49, 314 (1953).

THE SPECTRAL DISTRIBUTION OF RADIATION FROM NONACTIVATED ZnS-CdS PHOSPHORS AS A FUNCTION OF TEMPERATURE

L. Drozd and V. L. Levshin (pp. 773-779)

Received 13 July 1960

The luminescence spectra of ZnS-CdS-NaCl 2% phosphors are investigated as the composition is varied from 100% ZnS to 100% CdS and the temperature is varied from -195 to $+180^{\circ}\text{C}$. Three emission bands are found. The first is observed over the entire range of temperatures and compositions. The second is observed at temperatures below -120°C , for CdS concentrations ranging from 5 to 95%. It reaches its maximum development for equal concentration of the components. The third band appears at 35% CdS and becomes more intense as the CdS concentration increases. All bands are shifted strongly towards longer wavelengths as the cadmium concentration is increased. A slight shift in the same direction is observed for the first band when the temperature is lowered. The origins and properties of the bands are discussed.

In 1926 Guntz¹ discovered a new class of luminors whose base material consisted of a mixture of ZnS and CdS. When this mixed matrix is activated by copper¹ and silver,² depending on the CdS concentration, phosphors are obtained luminescing in all regions of the visible, starting with the blue.

Nonactivated ZnS-CdS phosphors also produce an intense luminescence which shifts towards the red as the CdS content is increased. A more precise investigation of the composition of the luminescence of ZnS-CdS:Cu phosphors as a function of cadmium concentration was carried out by Fridman and one of the authors.³ In that paper, a quantitative relationship was established between the CdS concentration (up to 30%) and the shift of the luminescence maximum. It was also found that the intensity of luminescence goes through a minimum for a CdS concentration of about 5%.

Since nonactivated mixed ZnS-CdS phosphors also show an intense luminescence, Bundel' and Rusanova⁴ questioned whether ZnS is activated by cadmium. However, we can consider the problem of the luminescence of mixed ZnS-CdS phosphors somewhat differently. Nonactivated ZnS exhibits an intense luminescence which is attributed to some natural centers. It is natural to assume that CdS contains a similar natural self-activator. Thus, from this point of view, two self-activators should be present in mixed ZnS-CdS phosphors. It is known that phosphors with two activators usually exhibit activator interaction which results in a change in phosphor properties. Three activators will interact in an activated ZnS-CdS base phosphor. The process therefore should be highly complex. In order to study the interaction of activators in ZnS-CdS phosphors, we should first settle the problem of the presence of a natural activator in CdS and its interaction with the ZnS self-activator in mixed phosphors.

A number of papers have already been devoted to the luminescence of single-activator ZnS and CdS phosphors. Since a self-activator is unquestionably present in ZnS, we shall not dwell on the papers devoted to this problem. In the literature, two luminescence bands are attributed to the one-component CdS phosphor. Red luminescence is observed in single crystals at room temperature.⁵ Some authors have also observed a green CdS luminescence; sharply differing opinions have been expressed concerning its origin.⁵⁻⁸

One of the present authors devoted a paper⁹ to the

problem of the existence of a self-activator in CdS, and its interaction with the ZnS self-activator in ZnS-CdS phosphors. In that paper the luminescence of ZnS-CdS phosphors was studied at room temperature. No specific radiation due to its self-activator was observed, even at 100% CdS. Thus it was not possible to show the existence of a CdS self-activator at room temperature. It was only possible to ascertain that the simple blue luminescence band corresponding to pure ZnS is slowly displaced when CdS is introduced into the lattice, in accordance with the change in lattice composition.

Among the work on the luminescence of nonactivated ZnS-CdS phosphors, we should also point out the investigations by Gisolf¹⁰ and Kroeger,⁶ which contain data concerning the fundamental absorption. Both authors have ascertained the existence of only one absorption band at any CdS content.

METHOD OF INVESTIGATION

In our study we used a series of 14 phosphor samples with different ZnS and CdS contents, from pure ZnS to pure CdS. The NaCl flux amounted to 2%. The phosphors were prepared in closed quartz crucibles and the batch was baked for 15 min in air at 900° . Analysis of the prepared phosphors showed that CdS losses during baking did not exceed 0.5% of the amount introduced, so that they could be ignored.

Excitation was effected by means of the 313, 365, and 436 m μ lines of mercury. The red radiation from the lamp transmitted by the filter for the 365 m μ line was eliminated by means of a $\text{CuSO}_4\cdot\text{H}_2\text{O}$ solution.

The stability of the PRK-4 lamp was rigorously controlled. To carry out observations in different temperature ranges, the wrapped samples were placed in an electric furnace mounted in a Dewar flask of special shape. To register the luminescence spectra, we used the PC-382 apparatus with two photomultipliers—the FEU-17 (for the 400-590 m μ range) and the FEU-22 (590-1200 m μ). We corrected the results for photomultiplier sensitivity and monochromator dispersion.

TEMPERATURE DEPENDENCE OF THE SPECTRA

We studied the luminescence spectra of the ZnS-CdS phosphor from -195° to $+180^{\circ}\text{C}$. No luminescence was

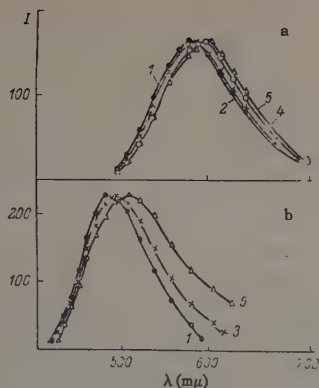


Fig. 1. Energy distribution in the spectrum of of ZnS-CdS phosphors (a—50% ZnS, 50% CdS; b—95% ZnS, 5% CdS) under excitation by $\lambda = 365\mu$ at different temperatures (in $^{\circ}\text{C}$). Curve 1— $+18^{\circ}$; curve 2— $+60^{\circ}$; curve 3— $+80^{\circ}$; curve 4— $+100^{\circ}$; curve 5— $+140^{\circ}$.

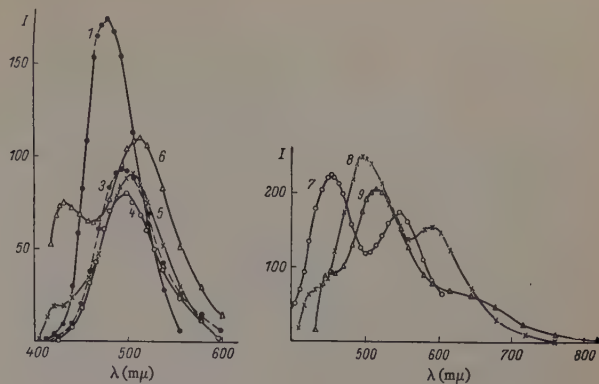


Fig. 2. Energy distribution in the spectra of ZnS-CdS phosphors at -195°C under excitation by 365μ radiation. Phosphor composition (percentage by weight): curve 1—10% ZnS; curve 3—95% ZnS, 5% CdS; curve 4—90% ZnS, 10% CdS; curve 5—85% ZnS, 15% CdS; curve 6—80% ZnS, 20% CdS; curve 7—65% ZnS, 35% CdS; curve 8—50% ZnS, 50% CdS; curve 9—35% ZnS, 65% CdS; curve 10—20% ZnS, 80% CdS; curve 11—10% ZnS, 90% CdS; curve 12—5% ZnS, 95% CdS; curve 14—100% CdS.

CdS content increases these bands also suffer a shift of the maxima towards longer wavelengths. The group II band does not appear in phosphors in which the CdS content exceeds 95%. Finally, a third group of bands (III) appears starting with the 50% ZnS-50% CdS phosphor. This group is also shifted with increasing CdS content.

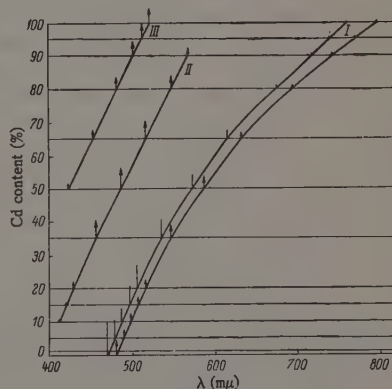


Fig. 3. Separation of series of luminescence bands in the spectra of ZnS-CdS phosphors at 18°C and -195°C .

observed above 180° . This indicates¹¹ the purity of the samples with regard to copper.

Figure 1 shows the spectra of two ZnS-CdS phosphors containing 5 and 50% CdS, respectively, at 60, 80, 100, and 140°C . The curves are normalized to the maxima of the luminescence curves at room temperature.

luminescence band with one minimum persists in both phosphors from 18 to 140°C , which indicates its simplicity. As the temperature is raised, the maximum of the band shifts slightly towards longer wavelengths. This shift is particularly noticeable for the 5% CdS phosphor. The same phosphor exhibits an enhancement of luminescence in the orange-red portion of the spectrum. Both of these effects are apparently connected with the transition of the phosphor from the sphalerite to the wurtzite modification. A similar effect was observed¹² for ZnS phosphors.

The one-band spectrum of the ZnS-CdS phosphors was also observed when the temperature was lowered to -120°C . New bands appeared when the samples were cooled below -120°C . Figure 2 shows the spectra of the entire series of phosphors at -195°C . Due to the complex nature of the spectra and to their gradual shifting, it is difficult to follow the changing positions and intensities of the individual bands in Fig. 2. We wanted to analyze and more concretely characterize the composition of the radiation of the individual phosphors and the position of their component bands as a function of phosphor composition. For this purpose we compared the luminescence curves in Fig. 3 in terms of two characteristic quantities, namely, the positions and intensities of the band maxima. The abscissa axis gives the wavelength in millimicrons, the ordinate axis on the left gives the percent CdS by weight. The intensities of the band maxima are represented by vertical lines at 18° and by arrows at -195° . The length of the line or arrow is proportional to the intensity of luminescence. As shown in Fig. 3, at -195° there are three distinct groups of bands in the spectra of the ZnS-CdS phosphors. The bands of the first group, denoted by the numeral I in Fig. 3, appear over the entire temperature range from -195° to $+180^{\circ}\text{C}$ and throughout the entire range of cadmium sulfide concentrations. As seen in Figs. 2 and 3, a new group of bands (II) appears starting at 10% CdS (more correctly with 5%, however, without the appearance of a maximum). As the

The solid lines in Fig. 3 show the positions of the maxima of I, II, and III bands as a function of CdS content. For I bands, this dependence is shown in Fig. 3 at both $+18^\circ\text{C}$ and -195°C . When the temperature is lowered from $+18^\circ\text{C}$ to -195°C , the maxima of the bands of group I are shifted towards longer wavelengths.

As shown in Fig. 3, the bands of groups II and III exist over a much narrower range of CdS concentrations. The II and III bands are shown in Fig. 3 only at -195° , since they appear only below -120°C .

Figure 4 shows the intensities at the maxima of I, II, and III bands as a function of CdS content at -195°C . The first band has a minimum at 10% CdS and a maximum at 35% CdS. A similar behavior was observed earlier⁹ by one of the authors for the nonactivated phosphor at 18°C , and also for ZnS-CdS:Cu phosphors. (See ref. 3.) It appeared reasonable to suppose that this behavior of the curve is connected with the gradual transition of the ZnS-CdS phosphors from the sphalerite to the wurtzite structure. In order to check this assumption we made Debye diagrams for the individual samples. These diagrams indicated the presence of both modifications in phosphors containing less than 50% CdS. We prepared several phosphors with CdS contents ranging from 0 to 20%, and baked them at 1200°C . At this temperature, only the wurtzite modification is obtained for ZnS as well as for all mixed phosphors. A study of the Debye diagrams showed that the new samples did have the wurtzite structure; they did not show the intensity minimum in the range 0-20% CdS. This confirmed the assumption stated above.

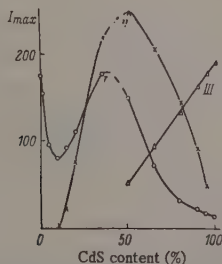


Fig. 4. Luminescence intensity at the maxima of bands I, II, and III of ZnS-CdS phosphors as a function of CdS content ($t = -195^\circ\text{C}$; exciting line $\lambda = 365 \text{ m}\mu$).

Figure 4 shows clearly the rapid growth of intensity at the maxima of type II bands up to 50% CdS content, followed by its rapid decrease. The intensity grows linearly for bands of group III, starting with their appearance at 50% CdS up to 100% CdS. The marked increase in the brightness of type II bands is accompanied by an equally marked weakening in the intensity of type I and II bands.

After studying the spectra of the ZnS-CdS phosphors at -195° , we investigated the temperature dependence of the intensities of type I, II, and III bands from -195° to $+180^\circ\text{C}$. The intensity at the maximum of each band was measured photoelectrically. A monochromator was used to isolate the approximate spectral region. To minimize the errors connected with the influence of the spectral shift when the temperature is lowered, the measurements were carried out with a wide monochromator entrance slit. The results are shown in Fig. 5. Band I is present throughout the entire temperature range and at all CdS concentrations. However, as the CdS content increases, the development of the band occurs at lower

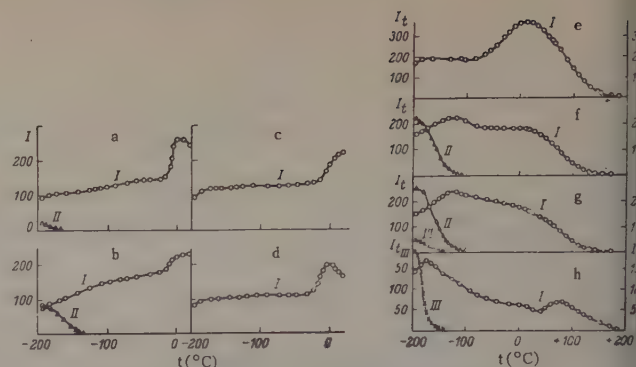


Fig. 5. Intensity of luminescence near the maxima of bands I, II, and III of ZnS-CdS phosphors as a function of temperature (exciting line $\lambda = 365 \text{ m}\mu$). Phosphor composition (percentage by weight) and measured positions of the maxima of bands I, II, and III (λ_I , λ_{II} , and λ_{III} in $\text{m}\mu$): a-85% ZnS, 15% CdS, $\lambda_I = 506.3$; $\lambda_{II} = 420$; b-95% ZnS, 5% CdS, $\lambda_I = 487$; c-80% ZnS, 20% CdS, $\lambda_I = 537.5$, $\lambda_{II} = 431$; d-90% ZnS, 10% CdS, $\lambda_I = 493.5$; e-100% ZnS, $\lambda_I = 481$; f-65% ZnS, 35% CdS, $\lambda_I = 556.5$, $\lambda_{II} = 453$; g-50% ZnS, 50% CdS, $\lambda_I = 589$, $\lambda_{II} = 493.5$, $\lambda_{III} = 416$; h-100% CdS, $\lambda_I = 800$, $\lambda_{III} = 521$.

and lower temperatures. The maximum development of band I is observed at $+20^\circ\text{C}$ for ZnS and at -175°C for CdS. Band II is a low temperature band. Its intensity falls rapidly as the temperature is raised from -195° . It disappears completely at -120°C . Band III is weakened rapidly with increasing temperature and becomes fully extinct near -145°C .

The development of the bands as a function of temperature was studied in more detail for the 50% ZnS-50% CdS phosphor. The spectra of this phosphor at different temperatures are shown in Fig. 6. As the temperature of the sample is raised from -195 to -120° , we observe a rapid weakening of band II and a simultaneous brightening of band I. When the temperature of the sample is increased still further, starting with -120°C , we observe the complete extinction of band II and a gradual weakening in intensity of band I.

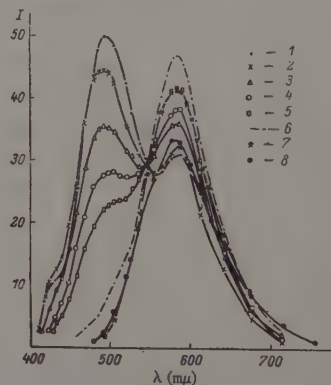


Fig. 6. Energy distribution in the spectrum of the 50% ZnS-50% CdS phosphor at different temperatures (exciting line $365 \text{ m}\mu$). Temperature (in $^\circ\text{C}$): 1-(-195); 2-(-180); 3-(-170); 4-(-160); 5-(-150); 6-(-120); 7-(-60); 8-(+18).

Change of Position and Intensity of the Emission Bands of ZnS-CdS Phosphors as a Function of ZnS and CdS Content

CdS (mol. %)	Band I						Band II		Band III		
	$t = 18^\circ \text{C}$			$t = -195^\circ \text{C}$			$t = -195^\circ \text{C}$		$t = -195^\circ \text{C}$		
	λ_{max}	I_{max}	λ_{max}	I_{max}	$\Delta\lambda$	λ_{max}	I_{max}	λ_{max}	I_{max}	λ_{max}	I_{max}
	(μ)		(μ)		(μ)	(μ)		(μ)		(μ)	
0	469	398	481	175	12	—	—	—	—	—	—
3.4	481	225	493	95	12	—	—	—	—	—	—
7	487	165	498	80	11	440	4.5	—	—	—	—
10.7	498	246	508.3	94	10.3	420	22	—	—	—	—
14.6	506	297	516	110	10	428	75	—	—	—	—
32.1	533	234	547	178	10	456	220	—	—	—	—
40.3	575	167	588.5	150	13.5	489	250	422	50	—	—
55.6	616	102	632	72	16	514	208	451	95	—	—
73	678	30	695	32	17	548	145	481	134	—	—
85.9	718	16	745	22	27	570	93	503.3	164	—	—
92.8	742	10	772	18	30	—	50	514	180	—	—
100	760	6	800	14	40	—	—	521	193	—	—

The Table contains quantitative data characterizing the positions of bands I, II, and III, as well as the intensities of the band maxima at 18 and -195°C .

The sample numbers listed in the first column correspond to the curve numbers in the drawings of Fig. 2 and also in ref. 9.

CONCLUSION

This investigation was devoted to the influence of the composition of the host crystal lattice on the composition of the radiation. We have shown the existence of three luminescence bands which develop in different temperature and composition ranges.

The change in composition of the crystalline lattice results in a change in the electrical field within the crystal. This may cause the following: (a) a change in the positions of the initial and final levels of the emission center and, correspondingly, a change in the position of the emission band; (b) a change in the probability of the corresponding transition. The first of these effects is noticed in all three bands. The second manifests itself in particular in the increase in nonradiative transitions when the lattice contains large inhomogeneities connected with its mixed sphalerite-wurtzite structure.

There is no doubt as to the nature of the emission centers of type I bands. These centers are formed by the natural ZnS activator. Types II and III bands appear only when CdS is introduced into the lattice. The follow-

ing facts have to be taken into account here: The maximum development of band II corresponds to an approximately equimolar concentration of ZnS and CdS. A further increase in CdS content causes this band to become weaker and simultaneously causes band II to become stronger, reaching its maximum at 100% CdS. We may therefore assume that we are dealing with the formation of two new types of centers. In the first case, both Zn and Cd enter into the composition of these centers in definite amounts; in the second case, only Cd. When the CdS content increases beyond 50%, there is a marked decrease in the number of the first centers and an increase in the number of the second. Our next communication will be devoted to a further study of the structure of the phosphors and their luminescence kinetics.

The authors wish to express their sincere appreciation to S. A. Fridman for consultations on phosphor chemistry and also to E. G. Vasil'eva and Z. Kozikhina for their cooperation and help in preparing the ZnS-CdS phosphor samples.

REFERENCES

1. A. A. Guntz, *Ann. chim (Paris)* **5**, 374 (1926).
2. S. Rotschild, *Z. Physik* **108**, 24 (1937).
3. V. L. Levshin and S. A. Fridman, *Zhur. Fiz. Khim* **6**, 1277 (1935).
4. A. A. Bundel' and A. I. Rusanova, *Izvest. Akad. Nauk SSSR, Ser. Fiz.* **13**, 173 (1949).
5. Y. T. Sihvonen, D. R. Boyd, and C. D. Woelke, *Phys. Rev.* **113**, 965 (1959); A. A. Vuylsteke and Y. T. Sihvonen, *Phys. Rev.* **113**, 40 (1959).
6. F. A. Kroeger, *Physica* **7**, 1 (1940).
7. E. Grillot, *J. phys. radium* **17**, 822 (1956).
8. G. Diemer, G. Gulp, and H. J. G. Van Meyer, *Physica* **23**, 987 (1957).
9. L. Drozd, *Izvest. Akad. Nauk SSSR, Ser. Fiz.* **23**, 1300 (1959).
10. J. H. Gisolf, *Physica* **6**, 84 (1939).
11. S. A. Fridman, A. A. Cherepnev, and T. S. Dobrol'yumskaya, *Doklady Akad. Nauk SSSR* **58**, 1341 (1947).
12. V. L. Levshin and V. F. Tunitskaya, *Opt. i Spektr.* **8**, 663 (1960), *Optics and Spectroscopy* **8**, 350 (1960).

Errata to Vol. 10 (February issue)

page	column	line	as printed	should be
87	2	15 from bottom	4	4,18
87	2	14 from bottom	18	19
87	2	10 from bottom	crystals	crystals ²⁰
87	2	7 from bottom	ref. 19.	ref. 20
87	2	bottom line	using an attachment described in ref. 20.	using an attachment.
88	1	16 from bottom	near 410°K^{21}	near 410°K

THE DETERIORATION OF A PHOSPHOR DURING ELECTROLUMINESCENCE

N. N. Grigor'ev and Yu. A. Kulyupin (pp. 780-786)

Received 11 July 1960

The process of deterioration of a ZnS-ZnO:Cu,Al,Cl electroluminor has been studied in a cell whose construction made it possible to change the disposition of the active particles without changing the effective volume or the conditions of excitation. The brightness of photoluminescence and electroluminescence, the intensity ratio of the "blue" and "green" bands, and the components of the light pulse were measured simultaneously at different stages of the deterioration process. According to these measurements, we may consider the phosphor damage to be local. It manifests itself to a greater extent at the surface and is not connected with any decrease in the number of luminescence centers. We observed changes in the frequency characteristic and in the dependence of brightness on voltage. The results obtained are explained satisfactorily by a decrease in the efficiency of the process of electroluminescence caused by growth of the space charge region.

It is of both theoretical and practical importance to ascertain the causes of the decrease in electroluminescent brightness which occurs with continued operation of an electroluminescent condenser, i.e., the deterioration process.

Roberts¹ and Thornton² indicate that this decrease in brightness is due to a change in the properties of the electroluminor itself. It is not clear, however, which properties do change. Roberts believes that there is a decrease in the number of luminescence centers, while Thornton assumes that the number of centers is invariant and that there is a change in the electrical properties of the phosphor; specifically, a decrease in the number of shallow donor levels which are ionized by the field. Both assumptions explain the experimental results satisfactorily. It is impossible, however, to give preference to either one on the basis of existing data.

The point of view presented by Roberts can be checked as follows: Since the same luminescence centers³ are responsible for both photoluminescent and electroluminescent processes, any change resulting in a decrease of the brightness of electroluminescence should also affect the brightness of photoluminescence. Thornton tried to perform such measurements;² however, as he pointed out himself, he did not achieve an unequivocal result, since in this experiment the decrease in the intensity of photoluminescence must be very small. The problem is more involved as regards the hypothesis proposed by Thornton, since it is difficult to study the electrical characteristics of a powdered electroluminor.

However, we can count on obtaining a definite answer from experiments connected with the storage of the light sum, since its magnitude should be affected by a change in the number of levels in the crystalline phosphor.

In order to study the correctness of the indicated hypotheses and to obtain additional information concerning the mechanism of electroluminor damage, we used a specially constructed demountable condenser. The arrangement is shown in Fig. 1.

Two transparent electrodes (1, 2) could be rotated with respect to each other without changing the spacing ($\sim 50 \mu$) between them. As a result of this operation, the phosphor crystals in the liquid dielectric were also partially turned. Thus, portions of crystals which previously did not luminesce were included in the operation.

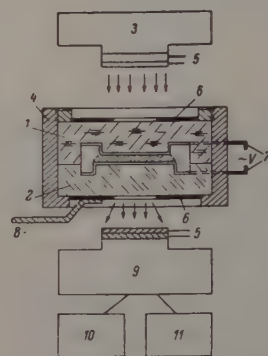


Fig. 1. The arrangement of the demountable condenser with movable transparent electrodes and a block diagram of the measuring system. 1, 2—transparent electrodes; 3—PRK-2 lamp; 4—frame with clamp; 5—filters; 6—diaphragm; 7—conducting layer contacts; 8—handle for turning the sample; 9—FEU = 19M photomultiplier; 10—M-95 microammeter; 11—ENO-1 oscilloscope.

This allowed us to create severe damage in an appreciable volume of the majority of the particles. The use of a diaphragm excluded the effect of new particles coming in from the edges.

We performed the experiments on a ZnS-ZnO:Cu,Al,Cl electroluminor* mixed with silicone oil. To accelerate

*The authors wish to express their gratitude to R. M. Medvedeva for preparing the electroluminor.

the process of deterioration, the phosphor was excited by an electric field with a 5×10^4 volts/cm gradient at a frequency of 15 kc. (We shall call this mode of excitation, in which the phosphor operates continuously, the "operating" mode. The term "measurement modes" will be used for other modes of operation during which various characteristics of the deteriorating phosphor were measured.) The output of the electroluminor was registered by a photomultiplier. The stability of the measuring arrangement was monitored by a continuously operating controlled light source. The blue and green emission bands were isolated by a system of crossed filters. Photoluminescence excited by light with

$\lambda_{\text{max}} = 3650 \text{ \AA}$ was registered in the green band (the fraction of the blue band passed by this filter was quite small). The constancy of photoexcitation was controlled by a lumogen.

First of all we ascertained whether the observed increase in brightness might not be due solely to changes in the dielectric. In this case a simple lowering of the applied voltage, with an equivalent decrease in brightness should cause all the changes characterizing the damage process. It turned out that the spectral composition of the radiation changed in the course of the deterioration.* (The green band/blue band intensity ratio of the transparency of the sample measured simultaneously did not change.

increased several-fold.²⁾ On the other hand, a lowering of the voltage to the brightness level of a phosphor which has been subjected to prolonged operation changed this ratio less than 10%. This shows that the process of deterioration is caused by a change in the properties of the phosphor itself. This conclusion agrees with the results of refs. 1 and 2, in which it was shown that the process of deterioration depends only slightly on the nature of the surrounding dielectric.

THE LOCAL NATURE OF THE DAMAGE

Since it has been established that the phosphor itself deteriorates, the question arises: where exactly does this damage occur—throughout the whole volume of the crystal or only at certain special locations? It is well known^{4,5} that an electroluminor excited by a field luminesces mainly at individual bright points. This is probably connected with the existence in the crystal of regions with a stronger field. We may assume that the damage also occurs mainly at these special locations. We could then expect a partial re-establishment of the brightness if the orientation of the particles with respect to the field were changed. (This would be due to the inclusion of fresh undamaged portions of the crystals.)

Figure 2 shows the sawtooth curve obtained for the brightness of phosphor luminescence by periodically changing the position of the electrodes. The figure clearly demonstrates the fact of phosphor damage, followed by recovery when the electrodes are turned. This indicates that the main deterioration does not occur throughout the whole crystal but only in certain special regions. The following results are obtained from measurements carried out during other measurement modes. The changes occurring in the phosphor are more strongly manifested

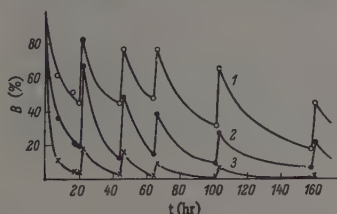


Fig. 2. Relative brightness measurements of phosphor electroluminescence (in the green band) in the course of deterioration when the electrodes are turned periodically. Measurement conditions: curve 1—400 cps, 240 volts; curve 2—15 kc, 240 volts (operating mode); curve 3—15 kc, 100 volts.

at lower voltages. This agrees with Roberts' results. Since the size of the brightly luminescing volume contracts with a decrease in voltage (and hence there is a decrease in the area in which damage is observed), this result indicates relatively serious deterioration of the phosphor as the region of maximum field is approached. This inhomogeneity emphasizes the local nature of the damage.

We can also try to demonstrate the local nature of the damage in a more concrete manner. The table contains data on the brightness of luminescence after each turn, expressed as a percentage of the initial brightness for different modes of measurement. The table shows that the degree of recovery is lower at lower voltages. This is understandable if we start from the assumption that the main deterioration occurs at the surface: After the turning of the crystal (i.e., after inclusion in the operation of undamaged areas) there is a higher percentage of damaged crystal area within the smaller luminescing volume at lower voltage. This conclusion agrees well with Goldberger's ideas⁶ concerning the localization of the barrier layer mainly on the surface of the electroluminescent crystals.

Intensity of the Green Band of the Deteriorating Phosphor After the Electrodes Are Turned

Measurement mode		Intensity after turn				
Voltage (volts)	Frequency (cps)	I	II	III	IV	V
240	400	82	76	76	65	45
	800	81	41	70	58	38
	15000	67	49	39	28	22
100	400	34	23	18	13	2.0
	800	29	21	16	12	1.8
	15000	18	16	9	7	1.5

Note. Operating mode—240 volts, 15 kc. Initial intensity in all cases is assumed to be 100%. The numerals I-V indicate the number of the turn.

INVARIANCE OF LUMINESCENCE CENTERS

Since the decrease in the brightness of phosphor luminescence is caused by a change in some of its properties, it is natural to assume that its luminescent properties are changed. We may consider, therefore, that either the luminescence centers are destroyed as assumed by Roberts,¹ that new centers appear with a high probability of nonradiative transition, or that both processes occur simultaneously. All of these effects should decrease the brightness of photoluminescence. Knowing the size of the volume in which luminescence occurs and ascribing all changes in intensity to the deterioration of luminescent properties in this same volume, we can determine the magnitude of the expected decrease in photoluminescence. We carried out a calculation for our case (240 volts and 15 kc) taking into account the number of turns made and the percentage of brightness recovery, and assuming a 10% effectively luminescing volume.* We

*This number is chosen in accordance with the results of refs. 3 and 7.

found that in the final state we should expect photoluminescence to decrease by 22%. This amount greatly exceeds the random error of measurements, which in our case amounted to 4%. Figure 3 shows the expected and the experimental values for the brightness of photoluminescence at different stages of the deterioration process. Since there is no decrease in the brightness of photoluminescence, we may conclude that the luminescent

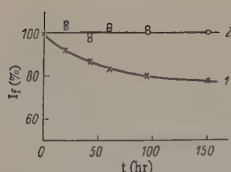


Fig. 3. The expected decrease of the brightness of photoluminescence (curve 1) and its experimental behavior (curve 2) at different stages of phosphor deterioration. Green band, operating mode—15 kc, 240 volts.

properties of the phosphor do not change in the process of deterioration. This forces us to look for the cause of phosphor deterioration in a change in other internal properties of the crystal.

SPREADING OF THE SPACE CHARGE REGION

A change in the electrical properties of the crystal might be expected to produce a sharp change in the brightness of luminescence under field excitation. Thus, to produce electroluminescence, it is very important to have a region of positive space charge arising under the action of the field and determining the magnitude of the field within the crystal. This region will increase in size if the space charge density decreases while the external field remains constant. Such spreading will decrease the field in the crystal and will result in a decrease both in the number of electrons capable of taking part in the luminescence and in their efficiency, thus causing a decrease in brightness. We should point out that it is impossible to cause such a decrease in the internal field by merely decreasing the external voltage applied to the crystal.

It can be shown that the results of the experiments can be explained on the basis of the spreading of the space charge region. This spreading is connected with a decrease in the positive space charge density ρ . If we assume, therefore, that the latter decreases uniformly throughout the whole deteriorating volume (which is a rough approximation), we see that as the damage increases, the quantity $b = b'/\sqrt{\rho}$, which enters into the well known expression $B = B_0 \exp(-b/\sqrt{V})$, also increases. This results in a change in slope of the brightness-voltage characteristic plotted on a semilogarithmic scale. Figure 4 shows clearly this increase in slope for a badly damaged sample. The experimentally observed smaller manifestation of damage at lower operating frequencies (which is clearly shown in Fig. 2 and in the

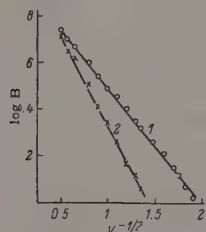


Fig. 4. Change of brightness-voltage characteristics in the course of deterioration of a phosphor in a solid dielectric. Green band, operating mode—15 kc, 320 volts. Curve 1—fresh layer; curve 2—after 200 hr.

table) also becomes to some extent understandable on the basis of the spreading of space charge. It is known⁸ that the average brightness of electroluminescence is mainly determined by the process of electron liberation through tunneling from deep traps at the boundary of the high field region. The time needed to surmount this potential barrier will depend on its width. It is obvious that if this time is to some extent comparable with the time during which tunneling may occur, i.e., with the period of the field, then the effect will be different at different frequencies. This is reflected in a certain sublinearity of the brightness-frequency characteristic and may possibly result in brightness saturation at high frequencies. Then the expansion of the space charge region and the corresponding increase in the time needed for electron liberation may bring about the observed change in the frequency dependence of a damaged phosphor.

If phosphor deterioration is connected with a change in the size of the space charge region, this should cause a change in the light pulses. This may be seen from a series of oscillograms (Fig. 5) which clearly show the decrease in the height of the fundamental peak (a_0) as compared with the secondary peak (a_g). When the electrodes are turned, this ratio tends to its initial value. This behavior of the amplitudes of the peaks is well explained by a decrease in the internal field caused by spreading of the space charge. Indeed, (a_0) is mainly controlled by the field⁹ and will be lowered by a decrease in the field. The amplitude a_g depends less on the field since its value is determined by the probability of thermal liberation of the available electrons.¹⁰ This is what causes a decrease in the value of the ratio a_0/a_g when both a_0 and a_g decrease simultaneously.

Furthermore, as operation continues, there is a change in the ratio of the ac and dc components of luminescence. According to present concepts,¹¹ the dc component at low frequencies is mainly due to luminescence occurring outside the space charge region. Then as the phosphor deteriorates, when the space charge spreads

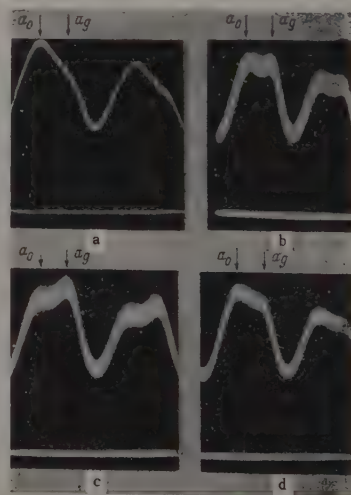


Fig. 5. Oscillograms of the change in shape of the brightness wave in the course of phosphor deterioration. Data for the green band at 400 cps, 240 volts (operating mode—15 kc, 240 volts). a—Fresh phosphor ($t_{\text{oper.}} = 0$ hr); b— $t_{\text{oper.}} = 20$ hr; c— $t_{\text{oper.}} = 90$ hr; d—electrode turned. Here a_0 is the fundamental peak and a_g the secondary peak.

here should be a decrease in the portion of the volume in which the dc component arises. This will cause it to decrease relative to the ac component. This process is clearly illustrated in Fig. 6.

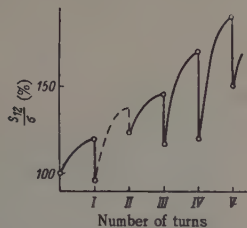


Fig. 6. Change in the ratio of the ac component S_{12} (area of peaks in both voltage half-periods) to the dc component σ of the light pulse (area under the ac component) at different stages in the course of deterioration. Green band at 400 cps, 240 volts (operating mode—15 kc, 240 volts). Oscillograms worked up assuming constant amplitude of the dc component σ .

Thornton has also observed a change in the shape of the light pulses.² He starts with the assumption that both the average brightness and the dc component are proportional to the number of ionized donor levels and considers that in the course of deterioration there is a decrease in the number of these levels within the crystal due to their destruction at the surface. He uses these considerations to explain both the sharp descent of the fundamental peak and the preferential decrease of the dc component. However, we consider such an explanation to be unsatisfactory.

In accord with the spectral changes of phosphor luminescence in the course of its deterioration, a certain difference is observed in the behavior of the brightness waves of the blue and green bands. Thus, for a fresh phosphor, the ratio of the ac to the dc component is greater for the blue band. As the phosphor deteriorates, there is a general increase in this ratio, and its values for the two bands become equal. This is understandable from the point of view of a contraction of the field-free region of the crystal where the luminescence is "greener." Furthermore, for a fresh phosphor, the secondary peak of the light pulse is practically absent in the blue band, while it is appreciable in the green band. As the phosphor deteriorates, this peak appears in the blue band but does not reach a high value. In the green band, the secondary peak becomes higher than the main one. The observed general "turning green" of the luminescence may possibly be connected with the indicated changes in the secondary peaks. It is difficult, however, without special quantitative calculations and measurements, to check the validity of this explanation of all the changes in the brightness waves of the two bands.

THE CAUSE OF SPACE CHARGE SPREADING

The increase in the rate of decrease of electroluminescent brightness with changing temperature² in the course of deterioration, as well as the occurrence of deterioration in the presence of a field and its increase with voltage, indicate the possibility of diffusion proc-

esses controlled by the field. Since a decrease in space charge density is essential for the spreading of the space charge region, we may assume that this is due to the drift of some charge formations (for example, of crystal defects ionized in the presence of the field). We may consider the following variations of this process: (1) the drift of defects existing in the crystal when their number decreases within the volume of the crystal; (2) the formation of new defects with somewhat deeper levels than existed in the crystal prior to deterioration.

As already noted above, we may try to draw a distinction between these two cases when we observe the change in the light sum stored before and after phosphor deterioration. Our observations concerning the onset of photoluminescence in a fresh phosphor and one in operation for a long time indicate some increase in the stored light sum in a damaged phosphor. This favors the second of these hypotheses. This comment, however, is only preliminary.

CONCLUSIONS

Our experiments allow us to draw the following conclusions:

1. The decrease of brightness with time is mainly caused by a change in the internal properties of the electroluminor, rather than those of the surrounding dielectric.
 2. Phosphor damage is localized and apparently occurs at the surface. (The latter circumstance may contribute to the effect of the dielectric on the decrease in brightness.)
 3. The luminescence centers remain unchanged in the course of phosphor deterioration. New centers characterized by nonradiative recombinations do not arise.
 4. The proposed mechanism for the decrease in brightness as being due to a spreading of the space charge region furnishes a qualitative explanation of the change in the dependence of brightness on voltage and frequency, the change in the shape of the light pulse, and the change in the luminescence spectrum which occur in the phosphor in the course of its deterioration.
 5. The cause of the spreading of the space charge region is not quite clear as yet. It is probably connected with the appearance of new localized capture levels whose depth somewhat exceeds that of the shallowest donor levels of the crystal. The surrounding medium may have some effect on the formation of these new levels.
- In conclusion, the authors wish to express their deep appreciation to M. V. Fok and V. V. Antonov-Romanovskii for valuable comments and discussion and to A. N. Savin for his help in this work.

REFERENCES

1. S. Roberts, *J. Appl. Phys.* **28**, 262 (1957).
2. W. A. Thornton, *J. Appl. Phys.* **28**, 313 (1957).
3. V. E. Oranovskii and Z. A. Trapeznikova, *Opt. i Spekr.* **5**, 303 (1958).
4. J. F. Waymouth and F. Bitter, *Phys. Rev.* **95**, 941 (1954).
5. A. Krehmeller, *J. Electrochem. Soc.* **107**, 8 (1960).
6. P. Goldberg, *J. Electrochem. Soc.* **106**, 34 (1959).

7. V. S. Trofimov, Opt. i Spekr. 4, 113 (1958).
8. A. N. Georgobiani and M. V. Fok, Opt. i Spekr. 10, 188 (1961), Optics and Spectroscopy 10, 95 (1961).
9. A. N. Georgobiani and M. V. Fok, Opt. i Spekr. 9,

- 775 (1960), Optics and Spectroscopy 9, 407 (1960).
10. C. H. Haake, J. Appl. Phys. 28, 117 (1957).
11. A. N. Georgobiani and M. V. Fok, Opt. i Spekr. 5, 167 (1958).

A METHOD FOR MEASURING SMALL OPTICAL ANISOTROPY

S. N. Pen'kov (pp. 787-791)

Received 22 June 1960

A photoelectric method for measuring small optical anisotropy is described, based on the separation from the total light beam of a component proportional to the phase difference δ . The method provides a large signal-to-noise ratio and permits reliable measurements of small values of δ in those cases where the anisotropy cannot be determined by the method of visual compensation. The application of the method is illustrated by several examples.

In measurements of small optical anisotropy in alternating and constant fields difficulties arise, connected both with unavoidable experimental conditions (imperfect Nicols, depolarization, etc.) and with the peculiarities of elliptically polarized light. In the visual method utilizing elliptical compensators the solution of this problem is connected with the fixation of a small light beam determined by the relation

$$\Phi = \frac{\Phi_0}{8} \sin^2 \varphi_1 \delta_1^2, \quad (1)$$

where φ_1 and δ_1 are respectively the azimuth of the sample under study and the phase difference between the ordinary and extraordinary rays, and Φ_0 is the light flux incident on the input Nicol. From Eq. (1) one can see the obvious difficulty in measuring azimuths and small values of δ , since the usable signal decreases with a decrease in anisotropy according to a square law. The application of half-covered compensators does not improve the experimental conditions, since in this case the measurement is based on the comparison of two light beams, one of which is determined by an expression analogous to that of Eq. (1).

Utilization of a photoelectric method permits one to obtain a signal proportional to δ_1 and not δ_1^2 .¹ In fact, if one places two plates between crossed Nicols, yielding phase differences δ_1 and δ_2 and characterized by azimuths φ_1 and φ_2 , then the light beam at the exit of the analyzer can be calculated in an elementary way, whereby its value is equal to

$$\Phi = \frac{\Phi_0}{2} \left\{ C_1 (\varphi_1 \varphi_2) \sin^2 \frac{\delta_1}{2} + C_2 (\varphi_1 \varphi_2) \sin^2 \frac{\delta_2}{2} \right. \quad (2)$$

$$\left. + \frac{1}{2} \sin 2\varphi_1 \sin 2\varphi_2 [\cos 2(\varphi_2 - \varphi_1) (1 - \cos \delta_1 \cos \delta_2) + \sin \delta_1 \sin \delta_2] \right\},$$

where C_1 and C_2 are trigonometric functions of the azimuths.

If one of the plates causes a phase difference determined by the expression

$$\delta_2 = \delta_{20} \sin(\omega t - \alpha), \quad (3)$$

and the photomultiplier receiving the light beam (2) is connected to an amplifier having a band width $\Delta f \ll \omega$, then the magnitude of a signal of frequency ω at the output of the amplifier will be expressed by the formula

$$V_{\omega} = \frac{AB\Phi_0}{4} \sin 2\varphi_1 \sin 2\varphi_2 \sin \delta_1 \sin \delta_2, \quad (4)$$

where the constants A and B are determined respectively by the properties of the amplifier and the photomultiplier. Thus, in this case the usable signal voltage is proportional to the first powers of the sine functions, in contrast with (1). From Eq. (4), it is seen that for a constant amplification factor the value of V_{ω} can become appreciable, if one increases the azimuth φ_1 of the auxiliary plate. From the symmetry of Eq. (4) it also follows that in the measurement of a small constant phase difference δ_1 the signal-to-noise ratio can be increased by means of an increase in the amplitude of δ_{20} of the accessory plate.

Elementary calculations show that the described method of signal amplification provides better conditions for the measurement of small anisotropy than the direct registration of the beam determined by Eq. (1). In fact, the noise at the output of the tuned amplifier is determined, fundamentally, by the noise of the photomultiplier since the latter is connected to the grid of the input tube. The root-mean-square value of the noise currents is determined from the familiar expression $\bar{I}^2 = B\Phi_2 \Delta f e$, where Φ_2 is the light flux received by the photomultiplier and e is the electronic charge.

If the measurement is of a small harmonic anisotropy δ_2 of a sample with azimuth $\varphi_2 = \pi/4$, and a "quarter-wave plate" is used as an "amplifier," with a small azimuth φ_1 , then from (4) we have

$$V_{\omega} = \frac{AB\Phi_0}{2} \varphi_1 \delta_{20} \sin(\omega t - \alpha). \quad (5)$$

The root-mean-square noise voltage is therefore equal to

$$V_1 = A \sqrt{B\Phi_0(k + \varphi_1^2) \Delta f e},$$

where k is the unextinguished fraction of the light flux. Thus, the signal-to-noise ratio is

$$\gamma_1 = \frac{1}{2} \sqrt{\frac{B\Phi_0}{e\Delta f(k + \varphi_1^2)}} \varphi_1 \delta_{20} \quad (6)$$

and grows with rotation of the "quarter-wave" plate, having a limiting value equal to

$$\gamma_1 = \frac{1}{2} \sqrt{\frac{B\Phi_0}{e\Delta f}} \delta_{20}. \quad (7)$$

equations (5) and (6) are represented graphically in Fig. 1.

In the case of the registration of the light flux (1) we have, after an obvious calculation,

$$\gamma_2 = \frac{1}{16} \sqrt{\frac{B\Phi_0}{k\delta_{fe}}} \delta_{20}^2, \quad (8)$$

from which

$$\frac{\gamma_1}{\gamma_2} = \frac{8\sqrt{k}}{\delta_{20}}. \quad (9)$$

Thus, in the example of amplification of usable signal by means of a "quarter-wave plate" that we have considered, it is expedient to establish during the measurement a small path difference δ_{20} and have a large parasitic light flux present.

An experimental test of Eq. (5) was carried out with the standard apparatus for the measurement of optical anisotropy. (An FEU-19 photomultiplier was connected to a selective amplifier,² an EO-7 oscillograph, and a measuring amplifier 28-IM were used as a signal indicator, and the light source was an SVDSH-250 lamp.) Variable birefringence in the liquid was created as a result of the Maxwell effect near a vibrating plate.³

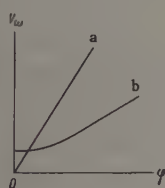


Fig. 1

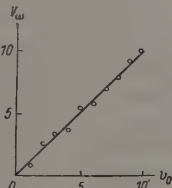


Fig. 2

Fig. 1. Dependence of usable signal voltage (curve a) and noise voltage (curve b) on the azimuth of the "quarter-wave plate."

Fig. 2. Dependence of usable signal amplitude on the amplitude of vibrational speed for phenyl-ethyl alcohol.

Figure 2 indicates, in arbitrary units, the dependence of signal amplitude V_{ω} for phenyl-ethyl alcohol on the amplitude of the vibrational speed v_0 of a glass plate, which is proportional to δ_{20} .⁴ An analogous linear dependence, but with other angular coefficients, is obtained from measurements on tetrabromomethane, toluene, and benzene. The experimentally determined function $V_{\omega} = V(\varphi_1)$ with $v_0 = \text{const.}$ corresponds to Eq. (5), if the azimuth of the "quarter-wave plate" does not exceed 2° . Otherwise, the measurements are made difficult by the presence of a high noise level caused by overloading the photomultiplier. The experiment showed that the signal V_{ω} , upon its amplification by a rotation of the "quarter-wave plate" within the indicated limits, was recorded on the screen of an oscilloscope in the case of an anisotropy that was at least 30 times less than the value determined by indication of the light flux (1), and corresponded to the case where visual measurement is impossible.

In distinction from the preceding case for the measurement of a constant, small anisotropy the method of elliptical modulation allows an absolute measurement of the quantity δ_1 . Let a plate with azimuth φ_1 , creating a constant small value δ_1 which we wish to determine, be placed between crossed Nicols. If we place before the analyzer an auxiliary plate, in which an anisotropy of the form (3) is excited, then from Eq. (4) (for the case $\varphi_2 =$

$\pi/4$) we have

$$V_{\omega} = \frac{AB\Phi_0}{4} \sin 2\varphi_1 \delta_1 \delta_{20} \sin(\omega t - \alpha). \quad (10)$$

Thus, the amplification of usable signal with $\varphi_1 \neq 0$ is possible by means of an increase in the amplitude of δ_{20} . Let us place between the plates an elliptical compensator with azimuth φ_3 , characterized by a small phase difference δ_3 . The state of polarization at the exit of the compensator is determined by the values of δ_1 , δ_3 , φ_1 , and φ_3 . It is obvious that for fixed δ_1 , δ_3 , and φ_1 there is a unique value of φ_3 for which the ellipticity of the beam coming out of the compensator will be extremely small. Hence the plates with indexes 1 and 3 can be replaced by one with a phase difference δ_1 , which is changed by rotation of the compensator. The equivalent phase difference has a deep minimum under the condition

$$\delta_1 = \delta_3 \sin 2\varphi_3. \quad (11)$$

The total anisotropy of these plates close to the minimum will equal

$$\delta'_1 \approx (\delta_1 - \delta_3 \sin 2\varphi_3). \quad (12)$$

In this case

$$V_{\omega} = \frac{AB\Phi_0}{4} \sin 2\varphi_1 (\delta_1 - \delta_3 \sin 2\varphi_3) \delta_{20} \sin(\omega t - \alpha). \quad (13)$$

Thus, the magnitude of V_{ω} when condition (11) is fulfilled reverts to zero, and the phase of the signal is changed by π . Analogous phenomena take place in the neighborhood $\varphi_1 = 0$, which appreciably increases the accuracy of the determination of δ_1 and the location of the optical axis of the sample under study.

The experimental possibilities of the method described became apparent in measurements of the Kerr constant in benzene and CCl_4 with the apparatus schematically indicated in Fig. 3.

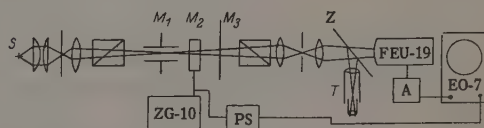


Fig. 3. Schematic diagram of apparatus for anisotropy measurement.

Here S is the light source, M_1 is a Kerr cell, M_2 is the elliptical modulator in which the harmonic anisotropy is set up, and M_3 is the compensator. The movable mirror Z and the optical tube T make it possible to carry out a visual measurement and necessary control. The receiving-amplifying part consists of the photomultiplier FEU-19, amplifier A, and audio generator ZG-10, the output of which causes the motion of the glass plate in the liquid.⁴ The phase shifter PS is connected to the horizontal input of the oscilloscope EO-7. The remaining parts of the setup are standard for apparatus of a similar nature (their designation is clear from the drawing).

If condition (11) is not satisfied, and $\varphi_1 \neq 0$, then an ellipse is seen on the oscilloscope screen, which changes into an inclined line when the knob of the phase shifter is turned (in case the value of δ_1 exceeds the threshold). The optimal operation conditions of the apparatus depend on the voltage of the audio generator, i.e., in the final analysis, on δ_{20} , which ought not to be very large. Otherwise overloading of the photomultiplier and a diminution of signal-to-noise ratio take place. Upon changing the

azimuth of the electric field or compensator in the vicinity of $\varphi_1 = 0$ and φ_3 according to (11), the line on the oscilloscope screen moves over from the quadrants 1-3 to 2-4. The horizontal position of the line corresponds to the condition of compensation, allowing the determination of the value of δ_1 and the position of the optic axis. For the measurements a Kerr cell with electrodes of length $l = 70$ mm and separation between them $d = 2$ mm was used.

Results of the measurements made with a compensator whose value of δ_3 was equal to 0.036 are shown in Fig. 4. By removing the modulator and suitably locating

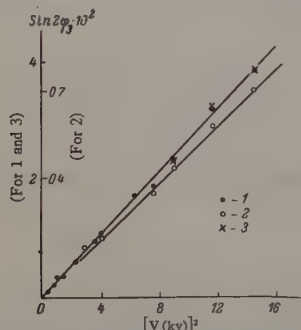


Fig. 4. Dependence of the anisotropy of liquid in a Kerr cell on the magnitude of the applied voltage. 1— C_6H_6 ; 2— CCl_4 (elliptical modulation method); 3— C_6H_6 (visual compensation method). $B(C_6H_6) = 0.5 \times 10^{-7}$; $B(CCl_4) = 0.09 \times 10^{-7}$. Scale on ordinate axis: left—for C_6H_6 ; right—for CCl_4 .

the mirror Z three measurements were also made on benzene, using the usual visual compensation method (those points shown by crosses in the figure). In this case the limiting value of anisotropy corresponds to the field which is obtained at a voltage $V \approx 2$ kv. Visual measurements at such field magnitudes are associated with large error. Points corresponding to values of $V^2 < 4$ (kv)² are obtained by the elliptical modulation method.

We note that for CCl_4 the anisotropy (for the values of E attained under the conditions of the experiment) was not observed visually. The coincidence of the values of the Kerr constant for benzene obtained by the visual compensation method and the method discussed here confirms the objectivity of the results. For the liquids investigated the value of the Kerr constant is found to be in satisfactory agreement with tabulated data.

In conclusion the author expresses his gratitude to V. N. Tsvetkov and E. V. Frisman for their continuous interest in the work and valuable suggestions.

REFERENCES

1. N. A. Tolstoy and P. P. Feofilov, *Doklady Akad. Nauk SSSR* **60**, 219 (1948).
2. A. M. Bonch-Bruевич, *Primenenie elektronnykh lamp v eksperimental'noi fizike* (The application of electron tubes in experimental physics), 1956, p. 270.
3. S. N. Pen'kov, *Opt. i Spektr.* **1**, 77 (1956).
4. S. N. Pen'kov, *Opt. i Spektr.* **10**, 653 (1961), *Optics and Spectroscopy* **10**, 343 (1961).

AN AUTOCOLLIMATION SYSTEM FOR PHOTOELECTRIC RECORDING OF HYPERFINE STRUCTURE

A. G. Zhiglinskii, A. N. Zaidel' and G. G. Kund (pp. 792-796)

Received 20 June 1960

A design for an apparatus with double passage of light through a Fabry-Perot interferometer is proposed for producing and photoelectrically recording high contrast interference patterns. The parameters of the equipment are investigated. For example, recordings of the hyperfine structure of lead lines indicate that the contrast of the interference pattern obtained with the proposed design is greater than is the case with designs ordinarily employed, even when using interferometer mirrors having high reflection coefficients.

Use of a Fabry-Perot interferometer to study weak components of hyperfine structure which occur close to strong ones requires a high degree of contrast, which is defined by the well known formula

$$C = \left(\frac{R+1}{R-1} \right)^2,$$

where R is the reflection coefficient of the mirrors.¹

The contrast increases with increasing R but the illuminating power of the interferometer falls off simultaneously.

Another way to improve the contrast is to use an apparatus consisting of two Fabry-Perot interferometers arranged in series with each other (the multiplex system). The contrast of a multiplex consisting of identical inter-

ferometers is equal to the square of the contrast of a single interferometer. Furthermore it is essential to match the thicknesses of both interferometers exactly and also, for photoelectric recording, the rate of change of the air pressure in their chambers must be accurately matched. In addition the interference patterns of both interferometers must be superimposed exactly. The fulfillment of all these conditions is sufficiently complicated that equipment of this kind is very sensitive to external influences.

If a multiplex consisting of two interferometers of identical thickness is replaced by a single interferometer with double passage of the light through it, the experimenter is freed to an appreciable degree from the difficulties mentioned above. Dufour has constructed an

paratus according to this principle in which photoelectric recording is used.² However Dufour's equipment does not make it possible to work in the central spot of the interference pattern. This circumstance leads to a loss of illuminating power and resolution when the spectra are recorded photoelectrically, and also introduces complication of the experimental techniques.³⁻⁷

The design proposed in this work (Fig. 1) is free of the disadvantages mentioned above. In this system light from the light source 1 is directed by a lens L_1 to the entrance aperture of the preliminary separation monochromator 2 (ISP-51). The lens L_2 transforms the light coming out of the monochromator into a parallel beam. The half of this beam not diaphragmed by the mirror M_1 passes through the appropriate half of the Fabry-Perot interferometer 3. The interference pattern is imaged by the lens L_3 onto the surface of the mirror M_2 . The diaphragm D_2 isolates the central part of the interference pattern and cuts off parasitic images of the entrance aperture of the monochromator. After reflection from the mirror M_2 and passage through the lens L_3 the parallel light beam passes through the second half of the interferometer 3. The mirror M_1 directs the light to the exit collimator and the lens L_4 images the interference pattern in the plane of the exit diaphragm D_3 which isolates the central spot of the interference pattern.

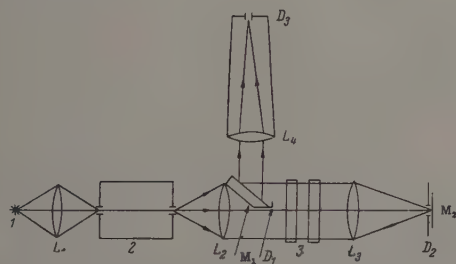


Fig. 1. Optical diagram of the equipment.

A photometer⁸ with an uncooled photomultiplier tube served as a light receiver in the apparatus described. All the optics were clear to reduce light scattering. The diaphragm D₁ prevented that fraction of the light reflected from the interferometer from falling on the exit collimator. Only the edge of the mirror M₁ had to be diaphragmed to a width of 1-2 mm. Scanning of the interference pattern was accomplished by changing the air pressure in the barochamber in which the interferometer was installed.

Since both light beams pass through the two halves of one and the same interferometer the difficulty of adjusting and matching thicknesses of the multiplex interferometers is eliminated. Light reflected from the first objective L_2 does not fall on the exit collimator in this system. The equipment is suitable for operation in the central spot. The parameters of the optical system were chosen in accordance with calculations carried out by Chaika.⁹

Let us compare the characteristics of ordinary systems with systems utilizing double passage of light. If it is assumed that the surfaces of an interferometer are finished to an accuracy of $\lambda/80$, then a reflection coefficient amounting to nearly 94%¹⁰ and a contrast $C = 1000$ can be realized with these surfaces. The transmission of such an interferometer is 44% when the absorption coefficient is 2%. However, Tolanskii¹ considers that in

practice contrasts no higher than 200 can be achieved at the present time in an ordinary system.

When contrasts greater than 200-1000 are required, of the equipment multiplex systems must be used. The latter provide the higher contrasts with loss in illuminating power (if the absorption is 2%) of approximately a factor of 5. In actual cases the loss of illuminating power is necessarily somewhat larger due to reflection and absorption in the auxiliary elements of the system with double passage of the ray (in comparison with an ordinary system).

The apparatus which we constructed according to the design described above (Fig. 1) included a Fabry-Perot interferometer with a coefficient of reflection $R = 85\%$ and an absorption coefficient $A = 2\%$ (such a choice was dictated by the fact that our equipment was intended for the solution of a specific problem; isotopic analysis of low concentrations of PB^{204}). Calculations for an ideal interferometer¹ yield in this case a value of 150 for the contrast of an apparatus with ordinary passage of light, a transmission at the maximum of the interference pattern of 76%, and a number of effective beams equal to ~ 16 .

The contrast of a system with double passage of light must be equal to the square of the contrast of an ordinary system, i.e., must amount to a value near 23,000. The transmission of the interferometer in our system is reduced to 25-30%. The number of effective beams and, consequently, the resolving power of the interferometer are increased by 1-1/2 times,¹ and for the example under consideration the number amounts to ~24. In use the system pictured in Fig. 1 can sharply increase the contrast of the interferometric arrangement at the expense of losses in illuminating power and can also obtain some gain in resolving power.

Higher contrast can be obtained also at the expense of increasing the reflection coefficients of the interferometer mirrors. It is easily calculated that, to obtain as much contrast as in the system described, an ordinary system would have to use mirrors with a reflection coefficient of 98.7%. At the present time however it is not possible to realize such a high reflection coefficient because of imperfections in the finishing of the interferometer surfaces. It should also be borne in mind that the realization of high reflection coefficients is accompanied by greatly reduced transmission of the interferometer.^{1,9}

The Pb I λ 4058 A line was chosen for the study of the constructed apparatus. This line was convenient for an investigation of the properties of the proposed system in view of the small doppler broadening of the lead line and the presence in the chosen line of hyperfine structure components which are sufficiently different in intensity. In addition to this the Pb 4058 A line, which serves in an analytical capacity in the isotopic analysis of lead by the spectral method, has been the subject of studies by a number of authors in the USSR and abroad, which facilitates comparison of the obtained data with the results achieved by ordinary systems.

A line of the isotope Pb^{208} λ 4058 Å which does not have hyperfine structure was used to study the apparatus contour. The lead sample was 85% enriched in the Pb^{206} isotope. In order to increase the apparatus broadening of the interferometer contour in relation to the doppler broadening, the study was conducted with the comparatively thin interferometer thickness of 5 mm and the light source (a hollow cathode) was cooled with liquid air. The reflection coefficient of the mirrors used in the inter-

ferometer was 85%; the absorption coefficient, 2%; and the accuracy of the surface finishing, $\lambda/10$. Under these conditions the width of the contour of the Pb I λ 4058 A line as recorded by the Fabry-Perot interferometer proved to be about 6 times greater than the calculated doppler contour of the line. A temperature of $T = 300^\circ\text{K}$ was used for the calculation.¹¹

As a result of the study of the contour of the Pb²⁰⁶ I λ 4058 A line with the ordinary system a contrast value of $C = 50$ was obtained and the number of effective beams N was 7 or 8. In the system with double-passed rays the contrast was increased so much that the intensity at the minimum of the interference pattern was too small for accurate measurements. Therefore, we established a lower limit for the contrast of the system under consideration. This limit was not less than 500 with a number of effective beams N amounting to 13 or 14. The increase in contrast and resolving power of the equipment was accompanied by a decrease by a factor of 8 in the illuminating power relative to the ordinary system.

A comparison of the theoretical and experimental data indicated that the calculated parameters of the system were not successfully realized for the mirrors used. It appeared that the most likely cause of this would be deviations from planeness of the mirror surfaces, so we tested an interferometer with the same coefficients of reflection and absorption but with the surfaces finished to an accuracy approximately an order of magnitude higher. As a result the contrast of the interference pattern obtained with the system under study increased by more than a factor of 4 (Fig. 2b and Fig. 2c) and became not less than 2000.

Chart recordings obtained under conditions of ordinary and double passage of light through interferometers with $R = 85\%$ and surface finishing accuracy $\Delta h \approx \lambda/10$ and $\lambda/100$ are shown in Fig. 2. Chart recordings obtained in this work and in ref. 12 using interferometers with $R = 92.5\%$ and 97% in ordinary systems are shown in this same figure for comparison (the Pb I λ 5201 A line studied by the authors of ref. 12 has isotopic displacement values close to the displacements of the Pb I λ 4058 A line which we investigated). In spite of the use of high reflection coefficients ($R = 97\%$), the contrast of the interference patterns obtained by them (compare chart recordings in Fig. 2c and 2e) was less than the contrast achieved in our work. A comparison of the chart recordings obtained with the results of other authors studying the hyperfine structure of the Pb I λ 4058 A line¹³⁻¹⁵ leads to the same conclusion.

The results obtained indicate the possibility of utilizing the system described in studies of weak components of hyperfine structure that are located near strong components. In particular, equipment of this type can be used for analysis of small concentrations of the Pb²⁰⁴ isotope, which is difficult to accomplish with an ordinary system.^{12, 16}

REFERENCES

1. S. Tolansky, "High Resolution Spectroscopy" Methuen & Co., London, 1947; Izd. Inostrannoi Lit., Moscow, 1955.
2. C. Dufour, Ann. phys. 6, 20 (1951).
3. C. Dufour and P. Jacquinot, J. recherches centre nat. recherche sci. lab. Bellevue (Paris) No. 6, 91 (1948).

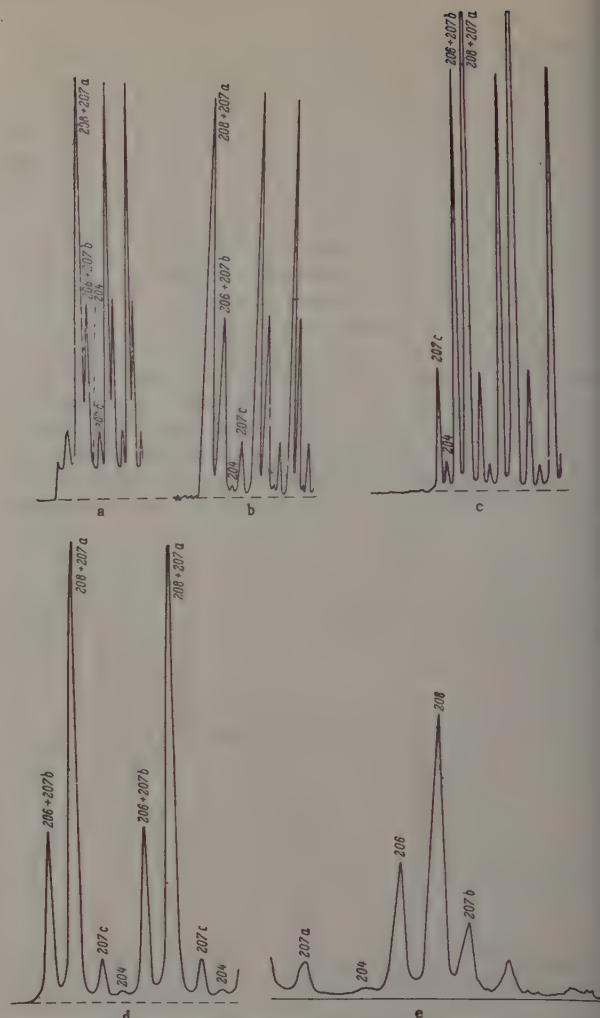


Fig. 2. Chart recordings of the hyperfine structure of lines of ordinary lead. a—Interferometer with $R = 85\%$ and $\Delta h \approx \lambda/10$ in an ordinary system; b—the same interferometer in a system with double-passed light; c—interferometer with $R = 85\%$ and $\Delta h \approx \lambda/100$ in a system with double-passed light; d—interferometer with $R = 92.5\%$ and $\Delta h \approx \lambda/100$ in an ordinary system; e—interferometer with $R = 97\%$ in an ordinary system. The thickness of the interferometer in the latter case was about 9 mm, in the others—15 mm.

4. R. Chabbal, J. recherches centre nat. recherche sci. lab. Bellevue (Paris) No. 24, 138 (1953).
5. P. Jacquinot, J. Opt. Soc. Am. 44, 761 (1954).
6. K. L. Vander Sluis and J. R. McNally, Jr., J. Opt. Soc. Am. 46, 39 (1956).
7. N. I. Kaliteevskii and M. P. Chaika, Vestnik Leningrad. Univ. No. 4, 9 (1956).
8. A. N. Zaidel', A. G. Zhiglinskii, and Yu. Chaiko, Czechoslov. J. Phys. 8, 539 (1958).
9. M. P. Chaika, Opt. i Spekt. 3, 372 (1957).
10. S. E. Frish, "Spectroscopic Determination of Nuclear Moments." Gosudarst. Ob'ed. Izd., Moscow, 1948.

3. A. N. Zaidel', N. I. Kaliteevskii, L. V. Lipis, and M. P. Chaika, "The Spectral Analysis of Atomic Materials," Gosudarst. Izd. Fiz.-Mat. Lit., Moscow, 1960.
4. J. Artaud, J. Blaise, and S. Gerstenkorn, Proc. 2nd Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1958.
5. J. K. Brody, M. Fred and F. S. Tomkins, Spectrochim. Acta 8, 329 (1957).
14. J. Blaise, Ann. phys. 3, 87 (1958).
15. M. S. Kashtan, E. V. Sobotovich, and T. N. Khlopina, Opt. i Spekt. 8, 24 (1960), Optics and Spectroscopy 8, 11 (1960).
16. A. N. Zaidel', A. G. Zhiglinskii, and Yu. Chaiko, Opt. i Spekt. 4, 152 (1958).

SHORT COMMUNICATIONS

VIBRATIONAL SPECTRA OF CERTAIN ORGANOMETALLIC COMPOUNDS OF THE GROUP IV ELEMENTS

N. N. Vyshinskii and N. K. Rudnevskii (pp. 797-799)

Received 25 July 1960

The organic compounds of tin and lead have lately acquired great theoretical and applied significance. However, their properties and structure still remain insufficiently studied.

In the present work, the infrared spectra of the following ethyl derivatives of tin and lead have been obtained: tetraethyltin ($(C_2H_5)_4Sn$), hexaethyldistannane ($(C_2H_5)_3Sn-Sn(C_2H_5)_3$), triethyltin oxide [$(C_2H_5)_3Sn)_2O$], methoxytriethyltin ($(C_2H_5)_3SnOCH_3$), dimethoxydiethyltin ($(C_2H_5)_2Sn(OCH_3)_2$) (Fig. 1), and tetraethyllead ($(C_2H_5)_4Pb$), hexaethyldiplumbane ($(C_2H_5)_3PbPb(C_2H_5)_3$), and triethyllead oxide [$(C_2H_5)_3Pb)_2O$] (Fig. 2). The Raman spectrum of hexaethyldiplumbane has also been obtained (Fig. 2d). The spectra of all the compounds listed have been investigated for the first time, with the exception of tetraethyltin and tetraethyllead, the spectra of which have been partially described in the literature.^{1,2}

The organotin compounds and oxygen-free lead compounds which we have investigated were obtained and purified by the methods described in refs. 3-7. Triethyllead oxide was kindly furnished us by Yu. A. Aleksandrov and T. G. Brilkina.

The absorption spectra were obtained using a ZMR-2 monochromator with a KBr prism and an IKS-2 spectrometer with a KCl prism. The Raman spectrum of hexaethyldiplumbane was obtained on an ISP-51 spectrograph with a camera of $f = 120$ mm; the exciting lines were the lines of the yellow mercury doublet.

Examination of the absorption spectra obtained shows that:

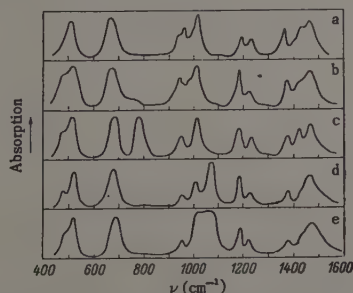


Fig. 1. Infrared spectra of $(C_2H_5)_4Sn$ (a); $(C_2H_5)_6Sn_2$ (b); $[(C_2H_5)_3Sn)_2O$ (c); $(C_2H_5)_3SnOCH_3$ (d); and $(C_2H_5)_2Sn(OCH_3)_2$ (e).

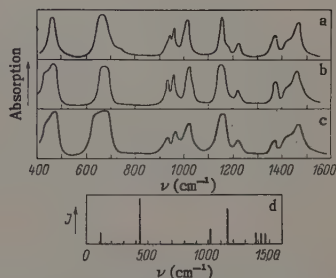


Fig. 2. Infrared spectra of $(C_2H_5)_4Pb$ (a); $(C_2H_5)_6Pb_2$ (b); $[(C_2H_5)_3Pb)_2O$ (c); and diagram of the Raman spectrum of $(C_2H_5)_6Pb_2$ (d).

(a) The compounds $(C_2H_5)_3SnSn(C_2H_5)_3$, $(C_2H_5)_3SnOSn(C_2H_5)_3$, $(C_2H_5)_3SnOCH_3$, $(C_2H_5)_2Sn(OCH_3)_2$, $(C_2H_5)_3PbPb(C_2H_5)_3$, and $(C_2H_5)_3PbOPb(C_2H_5)_3$, in which the tetrahedral symmetry of the set of atoms joined directly to the tin or lead atom is destroyed, have an absorption band in the 480 cm^{-1} region for the tin compounds and in the 440 cm^{-1} region for the lead compounds.

(b) In the spectrum, triethyltin oxide and triethyllead oxide give very intense absorption bands, which are lacking in the spectra of all the other compounds, in the 776 and 630 cm^{-1} regions respectively.

(c) The compounds $(C_2H_5)_3SnOCH_3$ and $(C_2H_5)_2Sn(OCH_3)_2$, which have a C—O bond, absorb very strongly in the $1050\text{--}1070\text{ cm}^{-1}$ region.

These peculiarities of the spectra may be explained on the basis of the following considerations.

1. Analysis of the literature data on the Raman spectra of tetraethyltin⁸ and tetraethyllead⁹ and comparison of the vibrational spectra of these compounds with the spectra of the tetramethyl derivatives¹⁰ allows us to assign the bands in the $470\text{--}515\text{ cm}^{-1}$ region in the case of $(C_2H_5)_4Sn$ and in the $430\text{--}460\text{ cm}^{-1}$ region in the case of $(C_2H_5)_4Pb$ to the stretching vibrations of the Sn—C and Pb—C bonds.

If we disregard the possibility of "free" internal rotation of the ethyl groups around the metal-carbon bonds, then the most probable equilibrium configuration of the $(C_2H_5)_4Sn$ and $(C_2H_5)_4Pb$ molecules will have the symmetry V_d (Fig. 3a). Then the frequencies 480 cm^{-1} for $(C_2H_5)_4Sn$ and 444 cm^{-1} for $(C_2H_5)_4Pb$ may be ascribed to the sym-

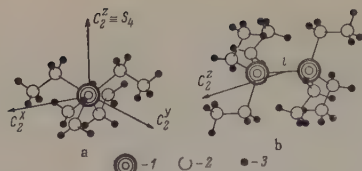


Fig. 3. Equilibrium configurations of the molecules $(C_2H_5)_4X$ (a) and $(C_2H_5)_6X_2$ (b). 1—X; 2—C; 3—H.

metrical stretching vibrations (A_1) of the central atom groupings SnC_4 and PbC_4 . The frequencies 508 cm^{-1} for $(C_2H_5)_4Sn$ and 460 cm^{-1} for $(C_2H_5)_4Pb$ belong to the unsymmetrical (B_2) and degenerate (E) vibrations of the same atom groupings, which are practically identical in frequency. The absence from the absorption spectrum of bands corresponding to vibrations of class A_1 agrees with the selection rules. On going over to compounds in which one or two ethyl groups on the central metal atom have been replaced, the over-all symmetry of the molecule is lowered, which finds expression in the spectra.

The symmetry C_{2h} may be assigned as most probable to the molecule $(C_2H_5)_3PbPb(C_2H_5)_3$ (Fig. 3b). The line with a frequency of 440 cm^{-1} found in the Raman spectrum is to be assigned to vibrations of class A_g . The absorption bands with frequencies 436 and 459 cm^{-1} belong to vibrations of classes B_u and A_u .

The corresponding absorption bands in the spectrum of $(C_2H_5)_3SnSn(C_2H_5)_3$ may be interpreted in just the same way.

An analogous picture is also observed in the spectra of $(C_2H_5)_4Si$ and $(C_2H_5)_3SiSi(C_2H_5)_3$.

In the case of $(C_2H_5)_3SnOCH_3$ and $(C_2H_5)_2Sn(OCH_3)_2$, the appearance in the absorption spectrum of two bands in the region of the $Sn-C$ stretching vibrations is also to be charged to the lowering of the symmetry of the molecules of these compounds in comparison with $(C_2H_5)_4Sn$.

2. The intense absorption bands with a frequency of 778 cm^{-1} in the spectrum of $(C_2H_5)_3SnOSn(C_2H_5)_3$ and 625 cm^{-1} in that of $(C_2H_5)_3PbOPb(C_2H_5)_3$, which differentiate the spectra of these substances from the spectra of the other compounds, are to be ascribed to the unsymmetrical stretching vibrations of the $Sn-O-Sn$ and $Pb-O-Pb$ groups—vibrations which establish the over-all C_{2v} symmetry of the molecules of the oxides under consideration.

The valence angle of the oxygen atom in these compounds is unknown, but one may assume that its value lies between the limits of 150 to 180° , since the $Si-O-Si$ angle in $(CH_3)_3SiOSi(CH_3)_3$, determined on the basis of spectroscopic data, equals 150° ,¹¹ and the volumes of the Sn and Pb atoms significantly exceed the volume of the Si atom. Such an assumption allows one to estimate approximately the magnitude of the stretching force con-

stant of the $Sn-O$ and $Pb-O$ bonds, on the basis of the valence force scheme¹² for $X-O-X$ triatomic models.

The calculation shows that the probable value of the stretching force constant for $Sn-O$ will lie in the interval 2.7×10^5 to 2.9×10^5 dynes/cm, and for $Pb-O$ in the interval 1.8×10^5 to 2.0×10^5 dynes/cm.

3. The intense absorption in the $1050-1070\text{ cm}^{-1}$ region in the spectra of $(C_2H_5)_3SnOCH_3$ and $(C_2H_5)_2Sn(OCH_3)_2$ is brought about by the $C-O$ stretching vibrations. An approximate calculation of the frequency of this vibration for the $Sn-O-CH_3$ model, carried out on the basis of data on the magnitude of the $k(C-O)$ force constant¹³ and the value found by us for $k(Sn-O)$, agrees with the assignment of the frequencies observed in the spectra to the $C-O$ vibrations and confirms the correctness of the interpretation of the frequency of the unsymmetrical $Sn-O-Sn$ stretching vibration in the spectrum of triethyl tin oxide.

The authors express their gratitude to G. A. Razuvaev for his interest in the work, and also thank N. S. Vyazankin for his help in the synthesis of certain compounds.

REFERENCES

1. H. D. Kaesz and F. G. A. Stone, *Spectrochim. Acta* No. 5, 360 (1959).
2. C. F. Kettering and W. W. Sleator, *Physics* 4, 39 (1935).
3. K. A. Kocheshkov, "Synthetic Methods in the Field of Organometallic Compounds of the IV Group," *Izd. Akad. Nauk SSSR, Moscow-Leningrad*, 1947.
4. T. Harada, *Sci. Papers Inst. Chem. Research (Tokyo)* 38, 115 (1940); *Chem. Abstr.* 35, 1027, 8 (1941).
5. G. P. Mack and E. Parker, *U.S. Pat.* 2700675, Jan. 25, 1955; *Chem. Abstr.* 50, P 397h (1956).
6. G. A. Razuvaev, N. S. Vyazankin, and O. A. Shchepetkova, *Zhur. Obshchei Khim.* 30, 2498 (1960).
7. G. A. Razuvaev, N. S. Vyazankin, and N. N. Vyshinskii, *Zhur. Obshchei Khim.* 29, 3662 (1959).
8. A. A. Baladin, E. I. Klabunovskii, M. P. Kozina, and O. D. Ul'yanova, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* No. 1, 12 (1958).
9. N. G. Pai, *Proc. Roy. Soc. (London)* A149, 29 (1935).
10. R. K. Sheline and K. S. Pitzer, *J. Chem. Phys.* 18, 595 (1950).
11. H. Kriegsmann, *Z. Electrochem.* 61, 1088 (1957).
12. M. V. Vol'kenshtein, M. A. El'yashevich, and B. I. Stepanov, "Molecular Vibrations," Vol. 1. Gosudarst. *Izd. Tekh. i Teoret. Lit., Moscow-Leningrad*, 1947.
13. K. Kohlrausch, "Ramanspektren," *Izd. Inostrannaya Lit., Moscow*, 1952. Edwards, Ann Arbor, Michigan

INFRARED ABSORPTION SPECTRA OF SODIUM DIHYDROGEN PHOSPHATE

A. I. Stekhanov, E. A. Popova, and A. A. Klochikhin (pp. 799-801)

Received 17 August 1960

Investigations of the Raman spectra of crystals of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ were undertaken in the work of ref. 1. In the spectra of these crystals, two broad washed-out bands were found in the 2000-3000 cm^{-1} region. Analogous bands have also been observed in the spectra of KH_2PO_4 , KH_2AsO_4 , and a number of other crystals. They are usually ascribed to a short hydrogen bond.² However, such an interpretation encounters a number of difficulties. Therefore, an effort was made in ref. 1 to explain the broad bands as second-order bands.

In this connection, great interest attaches to detailed investigations of the infrared absorption spectra of such crystals, especially of sodium dihydrogen phosphate, and also of its aqueous solutions. Such investigations have been carried out in the present work.

The infrared absorption spectra were recorded by means of an IKS-12 infrared spectrometer with a fluorite prism. Transparent suspensions of dihydrogen phosphate powders in organic oils were used as objects of study. Anhydrous NaH_2PO_4 was prepared from $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ by heating the latter to 130°C in vacuo. Concentrated aqueous solutions of sodium dihydrogen phosphate were investigated in a special cell with fluorite windows.

The infrared absorption spectrum of an $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ crystal is represented in Fig. 1. As can be seen from the figure, five narrow absorption bands with frequencies of 3262, 3316, 3390, 3448, and 3560 cm^{-1} are clearly observed in the region from 3200 to 3600 cm^{-1} . It is not difficult to notice that the first four of the narrow bands enumerated form two doublets with the same separation between the components (about 58 cm^{-1}). The 3560 cm^{-1} band, which is located apart, is noticeably narrower than the others. In addition to the narrow bands just considered, two more broad bands with maxima at 2600 and 2750 cm^{-1} are observed in the $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ spectrum (Fig. 1).

The infrared absorption spectrum of NaH_2PO_4 is represented in Fig. 2 (curve a), from which it can clearly be seen that, in the region under study, the spectrum of anhydrous sodium dihydrogen phosphate consists of only two broad washed-out bands with the frequencies 2370 and 2780 cm^{-1} .

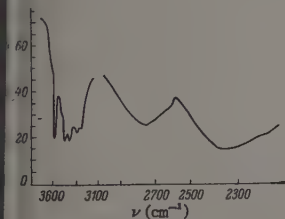


Fig. 1

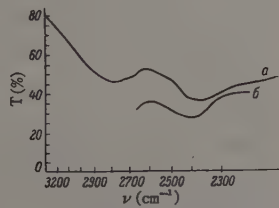


Fig. 2

Fig. 1. Infrared absorption spectrum of a crystal of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$.

Fig. 2. Infrared absorption spectra of NaH_2PO_4 in the crystalline state (curve a) and in aqueous solution (curve b).

We have studied the infrared absorption of aqueous solutions of NaH_2PO_4 in the frequency interval from 2000 to 2600 cm^{-1} . We did not succeed in investigating the higher-frequency region of the spectrum on account of the strong characteristic absorption of water. In Fig. 2 is presented the absorption curve (b) of a solution of sodium dihydrogen phosphate, from which it follows that, in the spectrum of the solution, there is a weak broad absorption band located around 2400 cm^{-1} .

At the present time, on account of the absence of reliable crystallographic data relating to the structure of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and NaH_2PO_4 crystals, a detailed interpretation of the infrared absorption spectra of sodium dihydrogen phosphate does not appear possible. However, the experimental results obtained from the spectra enable us to draw certain important conclusions concerning the characteristics of the hydrogen bond in these crystals.

It follows from a comparison of Figs. 1 and 2 that the infrared absorption spectra of the sodium dihydrogen phosphates in the 2000-3000 cm^{-1} region are identical. The two broad bands observed in the $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ spectrum are like the corresponding NaH_2PO_4 bands both in appearance and in their position in the spectrum. Similar absorption bands are also present, obviously, in the infrared spectrum of an aqueous sodium dihydrogen phosphate solution. One of these bands (the long-wavelength one) was definitely found in the spectrum, as can be seen from Fig. 2b. As for the second band, it falls in the region of the characteristic absorption of water.

Taking account of what has been set forth above, it is not difficult to reach the conclusion that the broad bands in all the spectra considered are of one and the same nature.

As has already been indicated, similar bands are also found in the spectra of ammonium dihydrogen phosphate,³ potassium dihydrogen phosphate,^{2,4} and certain other crystals. These bands, as has already been noted, are usually referred to a short hydrogen bond.⁴ However, an explanation of our results from this point of view encounters a number of difficulties. In fact, if we consider that the bands in the 2000-3000 cm^{-1} region belong to a hydrogen bond, then we must *ipso facto* assume the existence of a short bond in the $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ crystal. But since the broad bands are also observed in the NaH_2PO_4 spectrum, it is necessary to assume that the short hydrogen bond is not broken even on dehydration of sodium dihydrogen phosphate. Furthermore, it must also be preserved in an NaH_2PO_4 solution, as follows from Fig. 2. However, such assumptions seem improbable to us. Actually, it has been shown in the study of Raman spectra that a change in crystal structure exerts a substantial effect on the vibrational spectra of the crystals. Still larger changes in the spectrum should evidently be expected on going from the crystal to the solution.

On the basis of what has been said, we consider that the broad bands observed in the spectra under consideration can hardly be interpreted as the manifestation of

a short hydrogen bond. The results obtained, it seems to us, confirm the assumption expressed in ref. 1, according to which the broad bands observed in sodium, potassium, and ammonium dihydrogen phosphates are to be assigned to combination vibration frequencies of the H_2PO_4^- ion.

It is natural to consider that the broad 2400 cm^{-1} band observed in the infrared absorption spectra of aqueous solutions of sodium dihydrogen phosphate also belongs to combination vibration frequencies of the H_2PO_4^- ion. When an NaH_2PO_4 crystal is dissolved in water,⁴ it dissociates, as is well known, predominantly into Na^+ and H_2PO_4^- ions with a small content of the HPO_4^{2-} ion.

The existence in the infrared absorption spectrum of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ of a $3200\text{--}3500\text{ cm}^{-1}$ band with a complex structure and of a single narrow band around 3560 cm^{-1} (Fig. 1) is to be associated, we think, with vibrations of the molecules of water of crystallization. The latter is indicated by the circumstance that these bands disappear on dehydration of sodium dihydrogen phosphate (Fig. 2).

The appearance in the spectrum of the narrow 3559 cm^{-1} band undoubtedly indicates the presence in the crystal lattice of OH groups which form a weak hydrogen bond. On consideration of the complex structure of the displaced band consisting of two doublets, one's attention

is drawn to the fact that a similar structure of the OH vibration band is also observed in the Raman spectrum.³ The position and width of the observed doublets coincide completely in the two cases. This peculiarity in the appearance of the complex structure of the OH vibration band in the spectrum of sodium dihydrogen phosphate finds its explanation if we assume that, in the $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ crystal, the potential energy of the proton may be represented by a curve with two unsymmetrical minima (this question has been considered in detail in ref. 5).

REFERENCES

1. A. I. Stekhanov, A. A. Klochikhin, *Vestnik Leningrad. Gosudarst. Univ.* No. 16, 141 (1960).
2. G. S. Landsberg and F. S. Baryshanskaya, *Doklady Akad. Nauk SSSR* **61**, 1027 (1948).
3. A. I. Stekhanov, *Izvest. Akad. Nauk SSSR, Ser. Fiz.* **21**, 311 (1957).
4. K. A. Miller and C. H. Wilkins, *Anal. Chem.* **24**, 1253 (1952).
5. A. I. Stekhanov and A. A. Klochikhin, *Fiz. Tverdogo Tela* **2**, 2932 (1960). *Soviet Phys.-Solid State* **2**, 2605 (1961).

REPETITIVE ACTION PULSED LIGHT SOURCE BASED ON ELECTRIC EXPLOSION OF WIRES

I. S. Marshak (pp. 801-804)

Received 30 September 1960

One of the possible ways of attaining very high instantaneous temperatures and pressures and obtaining high intensity light flashes is based on the explosion of fine wires by discharging a capacitor.¹⁻¹¹ The literature on exploding wires has been concerned principally with the physics of the transition of the wire from the solid to the vapor state, and is almost devoid of any information on the problems associated with using a pulsed discharge in the vapor of an exploding wire as a light source.* The

*Intensity data given in refs. 4 and 5 cannot be used since in the first of these papers the conditions under which the flash was obtained are not described, and the second paper contains obvious errors.

purpose of this paper is to fill this gap in the literature.

The gaseous discharge which appears after an interruption of the current, during which there is a decrease in the density of the metal vapor, is characterized by a very high voltage drop. Consequently the discharge channel has a considerable ohmic resistance R which decreases with time only as a result of an increase in diameter. A comparison of data on the increase of resistance with information obtained by image scanning of the channel width indicates that the discharge plasma has an almost constant resistivity of about 10^{-2} ohm-cm for an electric gradient of about 10^2 volts/cm , regardless of the material from which the wire was made. This value agrees with the magnitude of the resistivity of discharge plasmas in pulsed discharge lamps.¹²⁻¹⁵ The high value of R produces a rapid damping of current oscillations in

the discharge circuit, so that about 70% of the energy stored in the capacitor is dissipated in the discharge channel.

It follows from Fig. 1 that the peak light intensity is also almost independent of the material comprising the wire; however, the amount of light produced by tungsten is considerably greater than that produced by copper, because of the greater afterglow of the tungsten discharge. A comparison of discharges in the vapors of various materials (bismuth, tungsten, iron, copper, molybdenum, nickel, platinum, lead, silver, tantalum, and aqueous solutions of the salts of germanium, potassium, sodium, rhenium, cerium, and zirconium) established that the discharges in tungsten and tantalum vapors have the highest (and approximately equal) light yield. Comparison with similar data for pulsed discharge lamps shows that the light yield in tungsten vapor* ($\sim 14\text{ lumen}$

*The magnitude of the light yield was computed with respect to the total electrical energy stored in the capacitor.

sec/joule) is 2 or 3 times lower than that of xenon discharge tubes ($\sim 25\text{--}45\text{ lumen sec/joule}$) and is several times greater than the light yield from an open spark discharge in air; it is about the same as the light yield of a spherical xenon pulsed discharge lamp used in the single, high energy flash mode of operation.¹⁶ The duration of light from the discharge in tungsten vapor is several times greater than the corresponding quantity for spherical lamps (for similar modes of operation).

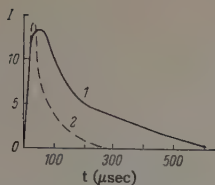


Fig. 1. Variation of light intensity (in megacandles) with time in the discharge of a $5 \mu\text{f}$ capacitor charged to 28 kv through tungsten (curve 1) and copper (curve 2) wires of 0.1 mm diam and 6 mm length.

The spectrum of the discharge is qualitatively similar to the spectrum of spherical lamps,⁹ which are characterized by a considerable increase of intensity with increasing wavelength (out to the transmission cutoff of quartz). This explains the lower light yield of these lamps in comparison to that of cylindrical pulsed discharge lamps, whose radiation spectrum peaks in the visible. However, the discharge in tungsten vapor can be an important advantage over pulsed lamps for certain problems, in that it allows one to obtain flashes of practically unlimited intensity with relatively short durations and small luminous area; these turn out to be intermediate between the dimensions of spherical and cylindrical lamps with approximately the same time-integrated intensity (Fig. 2).

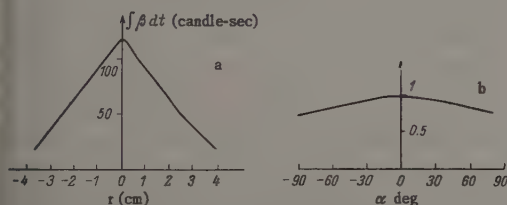


Fig. 2. Spatial distribution of the time integral of discharge channel brightness for a cross section perpendicular to the channel axis (a) and the angular distribution of discharge illumination in a plane passing through the axis (b) (in relative units). Tungsten wire 125 μ diam wound around a glass fiber in a spiral with a pitch of 1 mm and interelectrode spacing 60 mm. Results obtained by discharging a $5.1 \mu\text{f}$ capacitor charged to 30 kv through this wire.

If the diameter d and length l of the wires are small, the light yield of the discharge in tungsten vapor increases linearly with these parameters. This increase practically comes to a halt at $d = 0.2$ mm and $l = 100$ mm for applied voltages of 5 to 40 kv and flash energies of up to 3 kJ. As the energy of the flash is changed from hundreds to several thousand joules, the voltage from 20 to 40 kv, and the inductance of the discharge circuit from 1 to several hundred microhenries, the light yield shows only insignificant changes.

The practical utilization of this kind of pulsed light source is made difficult by the complexity of changing the wire in the discharge gap which would be needed for repetition of the flashes. During the course of the work described in this paper, a simple method was found for overcoming this difficulty. During the investigation of discharges in vapors of various metals, besides wires, cotton threads saturated with aqueous solutions of various

metal salts were also used. In this case, the discharge seemed to proceed in the same way as it did in the case of the wires (the solution first vaporized and then an intense pulsed discharge occurred in its vapor). However, because of the short duration of the discharge, the thread remained whole after the discharge. On the basis of this observation, experiments were attempted with discharges through metallic wires wound in spiral form around threads of insulating material.* It was found that after

*The winding can be done on machines for making wire spirals, such as the machines found in incandescent lamp factories.

an intense discharge the thread remained intact. An automatic apparatus for changing the wire was therefore constructed as shown schematically in Fig. 3. When switch 11 was closed, the section of wire between cylindrical electrodes 1 and 2 was vaporized instantaneously and a pulsed discharge took place in the metal vapor between the electrodes. After the discharge the metal vapors were dispersed, but the insulating core onto which the wire spiral was wound remained intact. By energizing the electric motor for a short time, a fresh section of the spiral wire was transported into the gap between the electrodes.

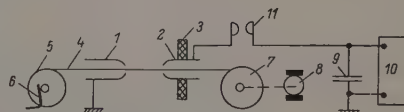


Fig. 3. Diagram of automatic wire feeder. 1, 2—cylindrical copper electrodes; 3—insulator; 4—thread wrapped with tungsten spiral; 5—drum containing reserve thread; 6—braking spring; 7—take-up drum; 8—electric motor and reducer; 9—capacitor containing the charge; 10—high voltage rectifier; 11—switch or auxiliary spark gap.

Various possible materials and dimensions were tried for the insulating thread and various values for the diameter and pitch of the tungsten wire windings were also tested.

Tungsten was selected as the material for the wire on the basis of illumination engineering considerations. Tests showed that the strength of a silk thread was greatly reduced after the spiral vaporized, but that the strength of a fiberglass thread remained the same. However, the winding of a tungsten spiral on a pure fiberglass thread produced scratches in the thread and weakened it before the wire had even been vaporized. This was not observed if the glass fiber was covered with lacquer before winding the spiral. The strength of threads from mixed silk and fiberglass was not as great as that of pure fiberglass coated with lacquer.*

*The strength of all the insulating threads decreased markedly if the discharge energy was not sufficient for an instantaneous vaporization of the wire and the formation of an intense gaseous discharge (the wire sputters in the form of droplets of the incandescent metal).

The use of the insulating core reduced the light yield of the discharge by 15 to 40%. Observation of the discharge by means of image scanning showed that this reduction could be partially explained by the fact that the core screens off part of the luminous layer. The slight (~10%) reduction in yield due to the lacquer indi-

cates that there is some effect traceable to the vapor of the core material.

On the basis of our investigations, the following thread characteristics can be recommended for flash energies of several hundred to several thousand joules: core material fiberglass, 128 gauge, covered by enamel lacquer; tungsten spiral—wire diameter 128 μ and a pitch of 1 turn per mm. Such a thread worked successfully at a winding rate of 30 cm/sec, tension of about 1 kg, and 1 to 5 sec interval between flashes.

REFERENCES

1. J. A. Anderson and S. Smith, *Astrophys. J.* **64**, 295 (1926).
2. I. S. Abramson and I. S. Marshak, *Zhur. Tekh. Fiz.* **12**, 632 (1942).
3. N. N. Sobolev, *Zhur. Eksptl. i Teoret. Fiz.* **17**, 986 (1947).
4. R. Heine-Geldern, E. M. Pugh, and S. Foner, *Phys. Rev.* **70**, 230 (1950).
5. W. M. Conn, *J. Opt. Soc. Am.* **41**, 445 (1951).
6. I. F. Kvartskhava, A. A. Plyutto, A. A. Chernov, and V. V. Bondarenko, *Zhur. Eksptl. i Teoret. Fiz.* **30**, 40 (1956).
7. M. O'Day, W. G. Chace, and E. H. Cullington, *Proc. Intern. Conf. Ionization Phenomena Gases*, 3rd, Ven. 1957, p. 784.
8. W. Mueller, *Z. Physik* **149**, 397 (1957).
9. M. P. Vanyukov and A. A. Mak, *Uspekhi. Fiz. Nauk* **66**, 301 (1958).
10. E. David, *Z. Physik* **150**, 162 (1958).
11. *Exploding Wires*, N.Y. Lond. (1959).
12. I. S. Marshak, *Uspekhi Nauch. Fot., Akad. Nauk SSSR Otdel. Khim. Nauk* **6**, 16 (1959).
13. I. S. Marshak, *Zhur. Eksptl. i Teoret. Fiz.* **16**, 703, 718 (1946).
14. S. I. Andreev and M. P. Vanyukov, *Doklady II Vsesoyuz. Soveshchaniyu Vysokoskorostnoi Fot.* (Proc. Second All Union Conference on High Speed Photography), Moscow, 1960.
15. I. S. Marshak and L. I. Shchukin, *Doklady II Vsesoyuz. Soveshchaniyu Vysokoskorostnoi Fot.* (Proc. Second All Union Conference on High Speed Photography), Moscow, 1960.
16. *Svetotekhnika*, No. 9, 32 (1960).

THE OCCURRENCE OF THE GREEN MgH BANDS IN THE FLAME SPECTRUM

E. D. Bugrim, A. I. Lyutyi, and V. S. Rossikhin (pp. 804-806)

Received 11 November 1960

The green bands ($\lambda = 5211$ Å) of the MgH molecule have been observed in the spectra of an arc burning between magnesium electrodes in a hydrogen atmosphere,¹ a discharge tube containing hydrogen and magnesium vapor,² solid magnesium burning in air,³ a high temperature oven containing solid magnesium oxide,⁴ and sun spots.⁵ These bands were not observed in the spectrum of a hydrogen-air flame at a $1:10^5$ Mg to gas concentration.⁶

We succeeded in producing MgH bands by introducing metallic magnesium vapor into the outer cone of acetylene- and hydrogen-air flames. The Mg vapor was obtained by heating a steel tube containing a combustion boat with molten metallic magnesium in an oven. The Mg vapors were introduced into the outer cone of the flame by a stream of argon gas. A green glow, in the form of a disc, was observed on the surface of the outer cone, where the stream came into contact with it. This emission seems to be steady when the Mg vapors have some optimum temperature. At low oven temperatures, the green glow is absent due to the low concentration of Mg vapor. But its intensity also decreases at high oven temperatures despite the high concentration of Mg vapor.

The spectra were photographed with a Hilger spectrograph (quartz optics) without any vertical diaphragming at the slit. This allowed us to obtain spectra not only of the green glow zone, but also of the sections of the flame above and below this zone. The spectrum consists of the following: green bands of MgH (5211 Å); a very bright Mg line (4571 Å) which belongs to the forbidden intercombination transition (3^3P-3^3S); the green (5183, 5172, 5167 Å) and ultraviolet (3838, 3832, 3829 Å) triplets of Mg; bands (3700 and 3820 Å) of MgOH; and also the Mg

resonance line (2852 Å). Graphs characterizing the variation of intensity of various components of the spectrum along the height of the flame are given in Fig. 1. Attention is called to the anomalous intensity of Mg 4571 Å. Under usual conditions, the Mg green and ultraviolet triplets are appreciably brighter (about 30-50 times) than Mg 4571 Å.^{6,7} In this case, the opposite is true: Mg 4571 Å is 50 times more intense than the magnesium triplets. From Fig. 1, it can also be seen that the MgH band, the Mg line (4571 Å), and the Mg ultraviolet triplet are observed only in the spectrum of the green spot zone. At the same time, the MgOH band and the resonance line (2852 Å) of Mg show almost no change in intensity beyond the boundaries of the green spot.

The rotational structure of the MgH band is only weakly developed. This indicates a relatively low temperature in the green spot region. This fact is also con-

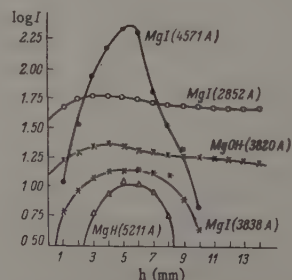
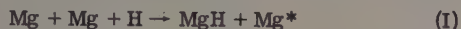


Fig. 1. Variation of the logarithm of the intensity of Mg lines and of MgH and MgOH bands with the flame height h . Intensity is expressed in relative units.

ated by thermocouple measurements of this section of flame, which gave a value of about 700°K. The weakening of the MgH band with increasing Mg vapor temperature, and also the localization of the MgH emission on the surface of the flame, where a sharp temperature drop exists, indicate that this molecule can be formed and can exist at relatively low temperatures. This conclusion is in agreement with the value of its dissociation energy, which is 2-2.5 ev.^{8,10}

In discussing these phenomena, it will be assumed that easily dissociable diatomic molecules are formed by means of three-body collisions, in which the third body carries away the binding energy of the molecule formed.¹¹⁻¹³ In the formation of MgH, such a triple collision can take place in the following reaction



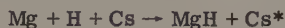
As a result of this process, the metastable state 3^3P of the Mg atom appears to acquire an anomalously high excitation, and consequently the forbidden line 4571 Å has a high intensity, as was observed in the experiment.

In order to verify the assumption about the energy change during process (I), an experiment was conducted on the following idea. If energy is transferred to a Cs atom, whose metastable level has an excitation potential of 2.71 ev, the same phenomenon would be expected to occur with any other atom having levels with excitation potentials close to 2.71 ev. Such an atom appears to exist in cesium, whose lines at 4555 Å and 4593 Å have excitation energies of 2.72 and 2.70 ev respectively. It is very fortunate that Cs possesses suitable levels, because in the flame spectrum, apart from these lines, there are no other Cs lines whose excitation energies differ appreciably from the value 2.71 ev (particularly the resonance lines 8521 Å and 8943 Å). This enables one to observe the behavior of several lines of one element along the height of the flame.

The introduction of Cs and Mg vapors was accomplished by first exposing the steel tube containing Mg to thermal decomposition products of CsNO_3 . When the tube was heated, the Cs atoms attached to the walls entered the stream of Mg vapor. The spectra were photographed with the same spectrograph. One half of its photometer was loaded with infra-840, and the other half with isochrom (65 GOST units) plates. Figure 2 shows the intensity variation of some spectral components with the height of the flame. It is easily seen that in the region of the green spot, Mg 4571 Å, Cs 4555, and Cs 4593 have sharply anomalous intensities. Beyond the limits of this zone, Cs lines (4555 and 4593 Å) have an intensity which corresponds to their thermal excitation in the

outer cone of the flame. In our case, this intensity is 74 times smaller than in the green spot region. The resonance lines Cs 8521 and Cs 8943 Å show practically no change in intensity.

Thus, the data obtained definitely confirm the existence of a mechanism for transferring the excitation, although they do not indicate which one of the following two processes actually occurs:



or



Attention is also called to the fact that the value of the Cs intensity ratio I_{4555}/I_{4593} is not constant along the height of the flame. As seen from Fig. 3, this ratio has its maximum value at the center of the green spot, and decreases smoothly toward its limb. Beyond the limits of the spot, it reaches a value which is equal to the ratio of the intensities of these lines at thermal excitation in the outer cone of the flame.

The results obtained do not contradict earlier observations, which state that the transfer of excitation energy from atoms A to B occurs with a greater probability when the excitation energy of the level of atom B is somewhat higher than that of atom A.¹⁴ It is also apparent that the ratio of these probabilities depends on the concentration of atoms in the metastable state (in our case $[\text{Mg}^*]$).

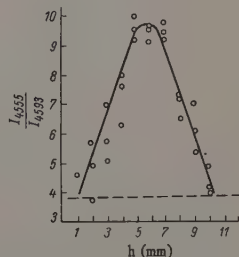


Fig. 3. Variation of the intensity ratio Cs 4555/Cs 4593 with flame height h . The horizontal line corresponds to the intensity ratio of these lines in the outer cone of the flame, without Mg.

REFERENCES

1. R. W. B. Pearse, Proc. Roy. Soc. (London) **A122**, 442 (1929).
2. A. Guntzsch, Z. Physik **93**, 534 (1935).
3. R. F. Barrow and D. V. Crawford, Proc. Phys. Soc. (London) **57**, 12 (1945).
4. L. Brewer and R. Porter, J. Chem. Phys. **22**, 1867 (1954).
5. A. Fowler, Phil. Trans. Roy. Soc. London **A209**, 447 (1909).
6. E. M. Bulewicz and T. M. Sugden, Trans. Faraday Soc. **437**, 720 (1959).
7. A. A. Zaidel', V. K. Prokof'ev, and S. M. Raikii, "Tables of Spectral Lines." Moscow-Leningrad, 1952.
8. G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules." Izd. Inostrannaya Lit., Moscow, 1949. 2nd ed., Van Nostrand, New York, 1950.

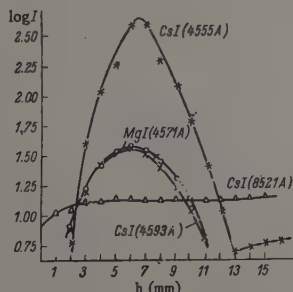


Fig. 2. Variation of the logarithm of intensities of Mg and Cs lines with flame height h . The intensities are expressed in relative units.

9. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," pp. 219-234. Wiley, New York, 1947. Chapman, London, 1947.
10. E. R. Lippincott and M. O. Dayhoff, *Spectrochim. Acta* **16**, 807 (1960).
11. E. M. Bulewicz and T. M. Sugden, *Trans. Faraday Soc.* **52**, 1465 (1956).
12. E. M. Bulewicz and T. M. Sugden, *Trans. Faraday Soc.* **52**, 1475 (1956).
13. E. M. Bulewicz and T. M. Sugden, *Trans. Faraday Soc.* **54**, 830 (1958).
14. S. E. Frish, *Izvest. Akad. Nauk SSSR, Ser. Fiz.* **3**, 431 (1936).

EFFECT OF SUPERPOSITION OF THE ABSORPTION SPECTRA OF THE COMPONENT BEING DETERMINED AND AN INTERFERING COMPONENT IN ABSORPTION SPECTRAL ANALYSIS

A. O. Sali' (pp. 806-808)

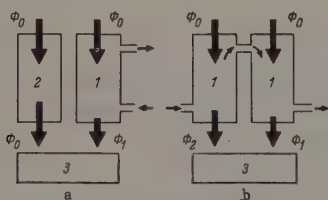
Received 16 December 1960

In addition to the component being determined in a mixture to be analyzed, there are often present other substances which absorb radiation (interfering components). We shall carry out a quantitative estimate of the error which arises when the content of an interfering component in the mixture to be analyzed is changed. Let ν be the frequency, $\kappa(\nu)$ and $\kappa_I(\nu)$ the respective individual absorption coefficients, and c and c_I the concentrations of the component being determined and of the interfering component in the mixture to be analyzed.

In a photometer (see figure) in which only one of the two strictly monochromatic beams being compared passes through the mixture to be analyzed (a), the quantity of radiation absorbed by this mixture depends on the sum $\kappa(\nu)c + \kappa_I(\nu)c_I$.¹ A change in the concentration of the interfering component by the amount Δc_I is perceived by the recording apparatus as a change in the concentration of the component being determined by the amount

$$\Delta c = \left[\frac{\kappa_I(\nu)}{\kappa(\nu)} \right] \Delta c_I \geq \left[\frac{\kappa_I(\nu)}{\kappa(\nu)} \right]_{\min} \Delta c_I,$$

where $[\kappa_I(\nu)/\kappa(\nu)]_{\min}$ is the minimum possible value of the ratio of the absorption coefficients, obtained by choice of the appropriate frequency ν . Actually, in consequence of the nonmonochromaticity of the beam, the magnitude of the error exceeds the minimum possible value shown on the right side of the inequality.



Basic designs of absorption analyzers. 1—cells with the mixture to be analyzed; 2—comparison cell; 3—differential radiation receiver, responding to the difference in the beams being compared.

Therefore we may set

$$\Delta c = a \left[\frac{\kappa_I(\nu)}{\kappa(\nu)} \right]_{\min} \Delta c_I, \quad (1)$$

where a is a coefficient depending on the choice of the

basic design and construction of the photometer.

For photometers in which one of the beams being compared passes through the mixture to be analyzed (see figure, a), the numerical value of the coefficient a approaches unity only in the ideal case (usually $a > 1$). For example, in infrared spectrophotometers where the spectral slit width is wide, exceeding the line width severalfold, the numerical value of the coefficient a attains a magnitude of the order of several units.² For the optico-acoustical gas analyzer,³ the value of a may be made less than 3 or 4 if a number of conditions are observed.²

To reduce the effect of the interfering component, photometers are used (see figure, b) in which both monochromatic beams (of different frequencies) being compared pass through the mixture to be analyzed.⁴ Let us choose the frequency of the right-hand monochromatic beam in such a way that the ratio $[\kappa_I(\nu)/\kappa(\nu)]$ is a minimum, and the frequency of the left-hand one so that the measured difference in the beams changes as little as possible with a change in c_I .

Let us generalize relation (1) to the case of the bichromatic photometer (figure, b). Let us denote by Φ_0 the fluxes passing into the receiver through the cells while light-absorbing components are absent from the latter, and by Φ_1 and Φ_2 the fluxes passing into the receiver when the component being determined is present in the cells at a concentration corresponding to the upper limit of measurement of the photometer. If the absorption coefficients change insignificantly within the spectral region delimited by the spectral slit width of the monochromator, then it is convenient to represent each of the total fluxes Φ_1 and Φ_2 in the form of a sum of two terms—the radiation delimited by the slit width, and the background radiation scattered by the monochromator. To a first approximation, one may consider that as the content of light-absorbing components in the mixture increases, the monochromatic term diminishes according to an exponential law, while the nonmonochromatic, background term remains practically constant. We shall consider, to a first approximation, that the ratio of this background radiation to the magnitude of the total flux Φ_0 equals δ for both the beams being compared. Then, assuming $\Phi_0 - \Phi_1 \ll \Phi_0$, we have for photometers which measure the flux difference directly (the readings of the recording apparatus are directly proportional to the difference being measured)

$$a \approx \left(1 - \frac{\Phi_1}{\Phi_0}\right) \frac{1}{(1-\delta)}.$$

For bichromatic photometers in which a method for measuring the ratio $(\Phi_2 - \Phi_1) \cdot \Phi_2^{-1}$ or the ratio $(\Phi_2 - \Phi_1^{-1})$ is used, we find

$$a \approx \left(\frac{\delta}{1-\delta}\right) \left(1 - \frac{\Phi_1}{\Phi_0}\right).$$

also obtain a similar expression for the coefficient in the case of a null-balance method of measurement.

When $\delta = 0.1$ and $\Phi_1 = 0.9\Phi_0$, we obtain $a \approx 10^{-2}$ for a bichromatic photometer (figure, b) with a null-balance method of measurement; i.e., when two monochromatic beams with different frequencies are used, the influence of an interfering component in the case under consider-

ation may be reduced by a factor of 10^2 (so long as there are no causes limiting the selectivity of the absorption analysis other than the overlap of the absorption spectra).

REFERENCES

1. V. M. Chulanovskii, "Introduction to Molecular Spectral Analysis," Gosudarst. Tekh. i Teoret. Izd., Moscow-Leningrad, 1950.
2. A. O. Sall', *Priborostroenie* No. 9, 12 (1956).
3. M. L. Veingerov, *Zavodskaya Lab.* No. 4, 426 (1947).
4. A. Savitzky and D. Bresky, *Ind. Eng. Chem.* **46**, 1382 (1954).

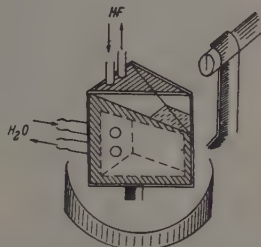
THE REFRACTION OF LIQUID HF

S. S. Batsanov and Yu. I. Vesnin (pp. 808-809)

Received 12 January 1961

Hydrogen fluoride is important in several reactions of theoretical chemistry but its electronic polarization is unknown. In addition, a knowledge of this quantity is essential for understanding the electronic interactions of atoms, for calculating the dipole moments, for the study of the hydrogen bond, and for other topics.

The difficulties in measuring the refractive index of liquid HF arise from its highly corrosive nature which necessitates special precautions in synthesizing it and special requirements on the optical materials.



Design of the apparatus for measuring the refractive index of HF.

We used thermal decomposition of KHF_2 to obtain anhydrous HF. The KHF_2 was first dried and purified by electrolysis in the molten state. The pure potassium bifluoride was heated in a platinum retort and the gaseous hydrogen fluoride generated was led through a teflon tube to a hollow prism of optical fluorite (angle $32^\circ 30'$). The prism was isolated from the air by a teflon cover which was partitioned off by a copper plate covered with a thin coating of teflon (see the figure). Water at a temperature of 10°C circulated in the lower part of the prism. In this way the HF was condensed in the prism itself, which was placed on the table of a GS-30 single circle goniometer.

The refractive index was measured in yellow light ($589\text{ m}\mu$, sodium lamp) and in red light ($674\text{ m}\mu$, interference filter). The angle of refraction α was almost the same in the two cases; four successive fillings and measurements gave a value of $\alpha = 5^\circ 39' \pm 2'$, corresponding to a refractive index of $n = 1.168 \pm 0.002$.

When the collimator slit is illuminated with white light, dispersion is observed but the displacement between the red and blue edges of the spectrum at minimum deviation does not exceed $4'$. This shows that the difference in refractive index does not exceed 0.002. Therefore, for the red portion of the spectrum we may use the value $n = 1.167$, for the yellow $n = 1.168$, and for the blue $n = 1.169$.

The value $n = 1.169$ is the lowest value recorded for the refractive index of an inorganic compound; according to Bleekrode's data,¹ ethylene has the lowest refractive index among liquified gases ($n = 1.180$).

The measured value of the refractive index of HF can be used to calculate its molecular refraction. Simon's data² give the following equation for the density of liquid hydrogen fluoride (t is the temperature in $^\circ\text{C}$):

$$d = 1.0020 - 0.0022625 \cdot t + 0.000003125 \cdot t^2$$

At 10°C this gives $d = 0.9797$. The molecular refraction $R_D = (M/d)(n^2 - 1)/(n^2 + 2) = 2.21\text{ cm}^3$. For $\lambda \rightarrow \infty$ we may use $n = 1.167$, giving $R_\infty = 2.20\text{ cm}^3$. It is interesting to note that Hannay and Smyth³ used a value of $R_D = 2.0\text{ cm}^3$ in calculations of the dipole moment of HF.

This value was obtained from the following simple considerations. Combining a proton with crystalline Cl^- , Br^- , and I^- ions lowers their refraction by 21.3%⁴ and with gaseous ions by 26.7%. This yields a value $R_{\text{HF}} = 1.76\text{ cm}^3$ (using $R_F = 2.40\text{ cm}^3$). However, this value corresponds to refraction by free hydrogen fluoride, while in the liquid state the HF molecule is combined in a chain of hydrogen bonds $\text{H}-\text{F} \cdots \text{H}$. The difference between the refractions $2.20 - 1.76 = 0.44\text{ cm}^3$ may be considered as a property of the H bond, or, in our terminology, the refraction of this hydrogen bond.

In ref. 4 it is shown that the greater the energy of a hydrogen bond the greater its refraction. The energy may be estimated, for example, in terms of the length and frequency of the H-F bond. Thus, the refraction of $\text{F}-\text{H} \cdots \text{F}$ in KHF_2 is 1.05 cm^3 ,⁴ and in liquid HF is 0.31 cm^3 . The lengths of the bonds are $2.26\text{ \AA}$ ⁵ and 2.49 - $2.55\text{ \AA}$,^{6,7} respectively. The vibration frequencies of the H-F bonds in these compounds are 3430 and 1450 cm^{-1} .⁸ Thus,

the refraction of the hydrogen bond increases with its strength. This correspondence is further confirmation of the validity of our determination of the refraction of liquid hydrogen fluoride.

REFERENCES

1. L. Bleekrode, Proc. Roy. Soc. **37**, 339 (1884).
2. I. Simons and I. Bouknight, J. Am. Chem. Soc. **55**, 1458 (1933).

3. N. Hannay and C. Smyth, J. Am. Chem. Soc. **68**, 171 (1946).
4. S. S. Batsanov, Zhur. Fiz. Khim. **34**, 68 (1960).
5. E. Westrum and K. Pitzer, J. Am. Chem. Soc. **71** (1949).
6. S. Bauer, J. Beach, and J. Simons, J. Am. Chem. Soc. **61**, 19 (1939).
7. M. Atoji and W. Lipscomb, Acta Cryst. **7**, 173 (1954).
8. K. Nakamoto, M. Mangoshes, and R. Rundle, J. Am. Chem. Soc. **77**, 6480 (1955).

LETTERS TO THE EDITOR

ON THE ARTICLE "THE ABSORPTION AND DISPERSION OF THIN GOLD FILMS" BY A. N. TEKUCHEV

I. N. Shklyarevskii (pp. 810)

Received 4 February 1961

An article in "Optics and Spectroscopy"¹ by A. N. Tekuchev was devoted to the determination of the dependence of the optical constants of gold films on their thickness. Such measurements, when carried out correctly, are of much interest.

It is well-known that thin (tens of Angstroms) metallic films have a granular structure and can be likened to a flat colloid. The size of the granules depends strongly on many factors: the nature of the evaporated metal, the rate of evaporation, the temperature of the substrate, the residual pressure, the thickness of the layer, etc. It is obvious for this reason that the effective values of the optical constants of such layers must be in some way related to the optical constants of the massive metal.

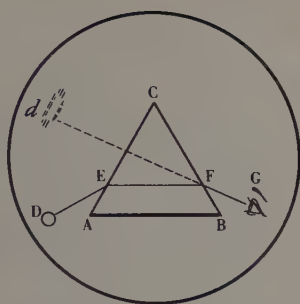
Because interference occurs in thin metallic films, the methods of measuring their effective optical constants μ_{eff} and $(\mu\kappa)_{\text{eff}}$ are radically different from the methods used for opaque layers. It is usual to measure the transmission coefficient T and the reflection coefficients R and R' from the air and the substrate sides, respectively^{2,3} at normal incidence. These depend in a complicated manner on the effective values of the optical constants of the film, the refractive indices of the adjacent media, the phase changes, and the thickness t of the film. The simultaneous solution of these equations (using graphical

methods) permits the quantities μ_{eff} and $(\mu\kappa)_{\text{eff}}$ to be determined. It should be mentioned here that according to Wolter⁴ in films below a certain thickness T , R and R' prove to be no longer independent of one another. In that case, in order to obtain μ_{eff} and $(\mu\kappa)_{\text{eff}}$ (and t) it is also necessary to measure the corresponding three phases (see, for example, refs. 5 and 6).

An error was made in the abovementioned paper by A. N. Tekuchev: the optical constants of thin gold films were "measured" using a method which is applicable only to opaque films. In passing I would like to mention that a calculation of the conductivity from the optical constants of gold in the visible part of the spectrum¹ is devoid of any meaning.

REFERENCES

1. A. N. Tekuchev, Opt. i Spekt. **7**, 93 (1959), Optics and Spectroscopy **7**, 55 (1959).
2. H. Murmann, Z. Physik **80**, 161 (1933).
3. D. Malé, Ann. phys. **9**, 10 (1954).
4. H. Wolter, Z. Physik **105**, 269 (1937).
5. H. Schopper, Z. Physik **130**, 565 (1951).
6. C. von Fraystein, Z. Physik **139**, 163 (1954).



optics and spectroscopy

volume x

OPTICAL SOCIETY OF AMERICA

AUTHOR LIST

VOLUME X: JANUARY-JUNE

(Numbers in parentheses refer to pages in Russian original)

Abarenkov, I. V., (487) 250
 Adamov, M. N., (276) 139
 Agarbiceanu, I. I., (297) 151
 Aleksandrovskaya, A. M., (27) 14
 Antonova, I. M., (693) 367
 Antonov-Romanovskii, V. V., (182) 92, (214) 107, (644) 339
 Anufriev, A. A., (177) 90
 Arvan, Kh. L., (272) 137

Bakhshiev, N. G., (717) 379
 Balashov, I. F., (540) 279
 Batsanov, S. S., (808) 429
 Baranova, E. G., (362) 182
 Belous, V. M., (649) 341
 Belousova, I. M., (410) 206
 Berezin, V. I., (457) 233
 Beridze, D. K., (240) 119
 Bezuglyi, V. D., (555) 289
 Biberman, L. M., (565) 297
 Blanaru, L., (297) 151
 Bobovich, Ya. S., (418) 212
 Bogomolov, A. N., (322) 162
 Borisevich, N. A., (589) 309
 Bratsev, V. F., (693) 367
 Brodin, M. S., (473) 242
 Broude, V. L., (634) 333
 Bugrim, E. D., (804) 426
 Bystrov, V. F., (138) 68

Chaika, M. P., (15) 7
 Cheban, A. G., (493) 253
 Chekula, I. A., (595) 312
 Cherkasov, A. S., (466) 238, (544) 282
 Chernevskaya, E. G., (640) 337
 Chumaevskii, N. A., (69) 33

Daukshas, V. K., (63) 31
 Deineka, P. G., (177) 90
 Draganescu, V., (297) 151, (301) 152
 Dragneva, G. I., (466) 238
 Dronov, A. P., (312) 157
 Drozd, L., (773) 408
 D'yachenko, N. G., (649) 341
 Dzhamagidze, Sh. Z., (583) 306

Eliashberg, M. G., (348) 174
 Ershov, A. G., (96) 46, (198) 100

Favorin, V. N., (91) 43
 Fedorova, E. O., (663) 348
 Feofilov, P. P., (142) 70
 Fok, M. V., (188) 95, (225) 112, (374) 188

Gastilovich, E. A., (595) 312
 Georgobiani, A. N., (188) 95
 Gerasimov, F. M., (104) 50
 Godnev, I. N., (27) 14
 Gordadze, G. S., (551) 287

Gorshkov, V. K., (759) 401
 Gotlib, Yu. Ya., (335) 168
 Gracheva, E. P., (595) 312
 Grekov, A. P., (555) 289
 Gribkov, V. I., (549) 285
 Gribov, L. A., (412) 208
 Grigoriev, B. A., (96) 46, (198) 100
 Grigoriev, N. N., (780) 412
 Grigorovich, R., (113) 54
 Gross, E. F., (417) 211
 Gurevich, D. B., (410) 206
 Gurevich, E. I., (767) 405
 Gurinovich, G. P., (750) 396

Ionesco-Pallas, N. J., (297) 151
 Izmailov, N. A., (767) 405

Kagan, V. K., (276) 139
 Kagan, Yu. M., (547) 284
 Kaminskii, M. G., (667) 350
 Kaplyanskii, A. A., (165) 83, (368) 185
 Kard, P. G., (384) 193
 Karklina, E. A., (697) 368
 Kashtan, M. S., (518) 266
 Khan-Magometova, Sh. D., (549) 285
 Kharitonova, O. P., (745) 394
 Khesina, A. Ya., (607) 319
 Khlopina, T. N., (518) 266
 Khovratovich, N. N., (589) 309
 Kirillova, I. V., (693) 367
 Kiseleva, N. K., (266) 133
 Kizel', V. A., (541) 281
 Klochikhin, A. A., (799) 423
 Klochkov, V. P., (559) 292
 Kolesova, E. G., (268) 135
 Kolesova, V. A., (414) 209
 Komanichu, N., (297) 151
 Korennoi, E. P., (570) 299
 Korolev, F. A., (398) 200
 Korol'kov, V. S., (3) 1
 Koronkevich, V. P., (268) 135
 Korostelev, Yu. S., (457) 233
 Koslov, V. P., (663) 348
 Kovelev, I. F., (707) 374
 Kovner, M. A., (328) 165, (457) 233
 Kozina, G. S., (91) 43
 Kozlov, Yu. I., (600) 315
 Kozyrev, B. P., (657) 345
 Kreingold, F. I., (417) 211
 Kristofel', N. N., (487) 250
 Kropotkin, M. A., (657) 345
 Kryzhanovskii, B. P., (682) 359
 Kubarev, S. I., (535) 276
 Kudinskaya, L. V., (335) 168
 Kukanov, A. B., (289) 147
 Kulyupin, Yu. A., (780) 412
 Kund, G. G., (792) 418
 Kuznetsova, T. I., (41) 20
 Kvaratskheli, Yu. K., (398) 200

Lazarev, A. N., (79) 37
 Levina, R. Ya., (63) 31
 Levitina, E. I., (135) 66
 Levshin, L. V., (759) 401
 Levshin, V. L., (362) 182, (505) 259, (773) 408
 Lisitsa, M. P., (48) 23, (157) 79
 Livshits, B. L., (145) 73
 Lubchenko, A. F., (379) 191, (477) 244, (727) 384
 Lutyi, A. I., (804) 426

Malkes, L. Ya., (557) 291
 Mal'tsev, A. A., (564) 295
 Malykh, V. D., (524) 269
 Manaila, R., (113) 54
 Mandel'shtam, S. L., (390) 196
 Marikhin, V. A., (232) 116, (512) 263
 Marisova, S. V., (473) 242
 Markovskii, L. Ya., (194) 98
 Marshak, I. S., (801) 424
 Maslennikova, A. G., (131) 64
 Mokeeva, G. A., (86) 41
 Moroz, L. P., (249) 124
 Moskvina, N. A., (368) 185
 Mukhitdinova, I. A., (561) 294
 Muratov, V. R., (540) 279, (561) 294

Nagornaya, L. L., (555) 289, (557) 291
 Nedler, V. V., (390) 196
 Neporent, B. S., (287) 146
 Nesterko, N. A., (270) 136
 Nikitin, E. E., (443) 227
 Nilov, E. V., (540) 279
 Norman, G. E., (565) 297

Odintsov, V. I., (403) 202
 Oganezov, K. A., (577) 303
 Onoprienko, M. I., (634) 333
 Orlov, B. I., (276) 139
 Ortenberg, F. S., (270) 136
 Ostrovskaya, G. V., (673) 353
 Ostrovskii, Yu. I., (8) 3, (429) 219
 Ovander, L. N., (420) 213

Panchenko, Yu. N., (55) 27
 Pankratov, N. A., (127) 61
 Parfianovich, I. A., (500) 257, (680) 358
 Penkin, N. P., (8) 3, (429) 219
 Pen'kov, S. N., (653) 343, (787) 416
 Pentin, Yu. A., (55) 27
 Permogorov, V. I., (541) 281
 Petrashen', M. I., (487) 250
 Petrov, A. A., (131) 64, (673) 353
 Pilipovich, V. A., (209) 104
 Pipinis, P. A., (676) 355
 Politov, N. G., (173) 87
 Popova, E. A., (799) 423

- libytkova, N. N., (266) 133
 ppin, R. Kh., (308) 155
 zhevuskii, A. K., (368) 185
 khbaum, Ya. D., (524) 269
 kov, A. V., (713) 377
 utian, S. G., (134) 65
 zumovskii, A. N., (15) 7
 znikova, I. I., (281) 142
 mbakh, V. P., (683) 360
 ssikhin, B. S., (804) 426
 zman, I. M., (354) 178
 lnevsky, N. K., (797) 421
 sinov, L. A., (177) 90
 skin, A. I., (220) 110
 skin, Ya. I., (343) 172
 znikov, B. D., (505) 259
 ll, A. I., (806) 428
 rzhevskii, A. M., (621) 326
 wchenko, A. N., (750) 396
 ablya, A. V., (617) 324
 akhparonov, M. I., (240) 119
 aripov, Z., (55) 27
 aka, E. F., (684) 360
 gorin, D. N., (595) 312, (600) 315
 apulo, G. P., (553) 288
 lyarevsky, I. N., (810) 430
 lyapochnikov, V. A., (265) 132
 ostakovskii, M. F., (595) 312
 ukhtin, A. M., (436) 222
 uraleva, E. I., (500) 257, (680) 358
 vvangiradze, R. R., (577) 303, (583) 306
 Slovetskii, V. I., (365) 132
 Slutsker, A. I., (232) 116, (512) 263
 Smirnova, R. I., (194) 98
 Snegirev, B. N., (328) 165
 Sobel'man, I. I., (134) 65
 Sobolev, N. N., (312) 157
 Sokolov, V. A., (177) 90
 Soloviev, K. N., (737) 389, (750) 396
 Soshnikov, V. N., (448) 229
 Spartakov, A. A., (177) 90
 Stanevich, A. E., (538) 278
 Stavitskaya, G. P., (343) 172
 Stekhanov, A. I., (348) 174, (799) 423
 Stolbova, I. V., (287) 146
 Strizhevskii, V. L., (48) 23
 Sushchinskii, M. M., (41) 20
 Sverdlov, L. M., (33) 17, (152) 76, (702) 371
 Sveshnikov, B., (426) 216
 Sveshnikov, B. Ya., (86) 41
 Sviridov, A. G., (312) 157
 Tatevskii, V. M., (63) 31, (564) 295
 Tatu, V., (297) 151
 Tenisheva, T. F., (79) 37
 Terenin, A. N., (617) 324
 Timchenko, A. I., (557) 291
 Timofeeva, V. A., (533) 275
 Tkachuk, A. M., (220) 110
 Tolstoi, N. A., (177) 90, (220) 110
 Toporets, A. S., (528) 272
 Treshchova, E. G., (55) 27, (63) 31
 Tsyashchenko, Yu. P., (157) 79
 Tuvikene, L. M., (284) 144
 Ulyanov, K. N., (565) 297
 Utyanskaya, E. Z., (138) 68
 Uvarov, V. A., (96) 46, (198) 100
 Vanyukov, M. P., (540) 279, (561) 294
 Vasil'ev, E. F., (127) 61
 Vember, T. M., (544) 282
 Vertsner, V. N., (120) 58
 Veselov, M. G., (693) 367
 Vesnin, Yu. I., (808) 429
 Viktorova, E. N., (279) 141
 Vinokurov, L. A., (225) 112, (374) 188
 Vorob'ev, Yu. V., (120) 58, (257) 128
 Vyshinsky, N. N., (797) 421
 Yagupolskii, L. M., (138) 68
 Yakovlev, E. A., (104) 50
 Yakovleva, T. V., (131) 64
 Yaroslavskii, N. G., (538) 278
 Zaidel', A. N., (15) 7, (570) 299, (673) 353, (697) 368, (792) 418
 Zaitseva, N. E., (272) 137
 Zakhar'evskii, A. N., (424) 215
 Zakharova, V. M., (547) 284
 Zhevandrov, N. D., (549) 285
 Zhiglinsky, A. G., (697) 368, (792) 418
 Zhmyreva, I. A., (281) 142

CONTENTS

VOLUME X: JANUARY-JUNE

(Numbers in parentheses refer to pages in Russian original)

No. 1—January 1961

- V. S. Korol'kov: The Size of Atomic Electron Shells as a Function of Atomic Number—(3) 1
- Yu. I. Ostrovskii and N. P. Penkin: Measurement of the Absolute Values of the Oscillator Strengths for the Resonance Lines of Calcium, Strontium, and Barium Ions—(8) 3
- A. N. Zaidel', A. N. Razumovskii, and M. P. Chaika: Spectral Determination of the Isotopic Composition of Lithium—(15) 7
- I. N. Godnev and A. M. Aleksandrovskaya: On the Use of the Curves $\nu = f(Z_X)$ in the Study of the Vibrational Spectra of Tetrahedral Molecules and Ions of the Form $X(\text{Hal})_4$ —(27) 14
- L. M. Sverdlov: Calculation of the Integrated Intensities of the Infrared Bands of Isotopically Substituted Methanes. VIII—(33) 17
- T. I. Kuznetsova and M. M. Sushchinskii: Calculation and Interpretation of the Vibrational Spectra of Isobutane—(41) 20
- M. P. Lisitsa and V. L. Strizhevskii: On the Temperature Dependence of the Intensities of Vibrational Absorption Bands in Gases—(48) 23
- Yu. A. Pentin, Yu. N. Panchenko, E. G. Treshchova, and Z. Sharipov: Infrared Absorption and Raman Spectra of Bipropenyl and Diallyl and the Question of Rotational Isomerism—(55) 27
- E. G. Treshchova, V. M. Tatevskii, V. K. Daukshas, and R. Ya. Levina: Raman Spectra of Various Classes of Hydrocarbons. VII. Ditertiaryalkylmethanes C_{10} – C_{17} —Branched Alkanes with Two Quaternary Carbon Atoms Separated by a Methylene Group—(63) 31
- N. A. Chumaevskii: Vibrational Spectra of Organic Compounds Containing Elements of Group IV (Si, Ge, Sn) I. Characteristic Absorption Bands in the Infrared Spectra of Silicon-Organic Compounds—(69) 33
- A. N. Lazarev and T. F. Tenisheva: The Vibrational Spectra of Silicates. II. Infrared Absorption Spectra of Silicates and Germanates with Chain Anions—(79) 37
- G. A. Mokeeva and B. Ya. Sveshnikov: On the Mechanism of the Transition of Excited Organic Molecules into the Metastable State—(86) 41
- V. N. Favorin and G. S. Kozina: Electroluminescence of a Powdered $\text{ZnS}:\text{Cu}:\text{Mn}$ Electroluminor in a dc Field—(91) 43
- B. A. Grigoriev, A. G. Ershov, and V. A. Uvarov: The Reflection of Radiation from an Infinite Flat Surface Illuminated by a Point Source. I. Characteristics of the Radiation Field—(96) 46
- E. A. Yakovlev and F. M. Gerasimov: Experimental Study of the Intensity Distribution in the Spectrum of Diffraction Gratings for Polarized Light—(104) 50
- Radu Grigorovich and Radika Manaila: The Effect of Object Thickness on Phase Contrast—(113) 54
- V. N. Vertsner and Yu. V. Vorob'ev: On the Chromatic Field Aberrations in Electron Microscopes—(120) 58
- N. A. Pankratov and E. F. Vasil'ev: Non Selective Optico-Acoustical Receiver of Radiation with a Capacitor Microphone—(127) 61

- T. V. Yakovleva, A. G. Maslennikova, and A. A. Petrov: On the Influence of the Nature of the Solvents on the Character of the Band of the Carbonyl Group in the Infrared Spectra of Carbonyl Compounds—(131) 64
- S. G. Rautian and I. I. Sobel'man: Remarks on Negative Absorption—(134) 65
- E. I. Levitina: Metallic Mirrors with an Enhanced Reflection Coefficient—(135) 66
- V. F. Bystrov, E. Z. Utyanskaya, and L. M. Yagupolskii: Magnetic Resonance Spectra of F^{19} in Aromatic Compounds with Substituents Containing Fluorine—(138) 68
- P. P. Feofilov: The Spectra and Luminescence Kinetics of $\text{CaF}_2:\text{Tb}$ Single Crystals—(142) 70

No. 2—February 1961

- B. L. Livshits: Effect of Free Rotation in Molecules on the Normal Vibration Frequencies—(145) 73
- L. M. Sverdlov: The Theory of the Intensities of Infrared Spectra of Polyatomic Molecules in the Zero and First Approximation of the Generalized Valence-Optical Scheme—(152) 76
- M. P. Lisitsa and Yu. P. Tsyashchenko: Temperature Dependence of the Vibrational Absorption Bands of Crystalline Chloroform and Bromoform—(157) 79
- A. A. Kaplyanskii: Band-Splitting in the Spectra of Cubic Crystals Subjected to Oriented Deformation—(165) 81
- N. G. Politov: The Complex Nature of the F-Band in KCl Crystals—(173) 87
- N. A. Tolstoi, A. A. Anufriev, P. G. Deineka, L. A. Rusinov, V. A. Sokolov, and A. A. Spartakov: Flashlike Rise of Luminescence II. $\text{ZnS}:\text{Co}$ and $\text{ZnS}:\text{Ag},\text{Co}$ Phosphors—(177) 90
- V. V. Antonov-Romanovskii: Final Stages of Luminescence Decay in Phosphors with Levels of Several Kinds—(182) 92
- A. N. Georgobiani and M. V. Fok: The Process Responsible for the Voltage Dependence of the Mean Luminescence Brightness—(188) 95
- L. Ya. Markovskii and R. I. Smirnova: The Luminescence Properties of Gold-Activated Zinc Selenide—(194) 98
- B. A. Grigor'ev, A. G. Ershov, and V. A. Uvarov: Reflection of Radiation by an Infinite Flat Surface, Illuminated From a Point Source. II. Particular Cases Important for Practical Applications—(198) 100
- V. A. Pilipovich: Polarization of Phosphorescence in Organophosphors—(209) 104
- V. V. Antonov-Romanovskii: Some Special Cases of Luminescence Kinetics—(214) 107
- N. A. Tolstoi, A. M. Tkachuk, and A. I. Ryskin: Flashlike Rise of Luminescence. III. Effect of the Intensity of the Exciting and De-exciting Light—(220) 110
- L. A. Vinokurov and M. V. Fok: Role of the Stimulating Action of Exciting Light in the Kinetics of Luminescence of $\text{ZnS}:\text{Cu}$ Crystalline Phosphors—(225) 112
- A. I. Slutsker and V. A. Marikhin: Certain Problems in the Theory of the Scattering of Electromagnetic Radiation by Submicroscopic Nonspherical Particles—(232) 116

- K. Beridze and M. I. Shakhparonov: Rayleigh Scattering of Light by Solutions of Nitrobenzene in Hexane—(240) 119
- P. Moroz: Imaging of Separate Linear Objects of Different Width and Contrast with Surrounding Field by a Combination of an Optical System and a Granular Layer—(249) 124
- V. Vorob'ev: An Analysis of Methods of Aligning Magnetic Electron Microscopes—(257) 128
- A. Shlyapochnikov and V. I. Slovetkii: The Use of Pressed Discs of KCl in Ultraviolet Spectrophotometry—(265) 132
- K. Kiseleva and N. N. Pribytkova: Determination of the Optical Constants of Ge and CdTe By the Reflection Method—(266) 133
- P. Koronkevich and E. B. Kolesova: Measurement of the Optical Density of the Blackening of Spectral Lines Using Interference Microscopy Methods—(268) 135
- S. Ortenberg and N. A. Nesterko: On the Effective Vibrational Temperature of the Acetylene-Air Flame—(270) 136
- L. Arvan and N. E. Zaitseva: Spectral Investigation of the Influence of the Solvent on the Aggregation of Organic Dyes—(272) 137
- N. Adamov, V. K. Kagan, and B. I. Orlov: Dispersion Formula for the Electron in a Potential Box of Finite Depth and the Optical Polarizability of Molecules—(276) 139
- N. Viktorova: Certain Regularities in the Nature of Yield Versus Fluorescence Band Position Functions for a Number of Organic Compounds—(279) 141
- A. Zhmyreva and I. I. Reznikova: The Influence of the Molecular Volume of a Solute on the Susceptibility of its Electronic Spectra to Solvent Effects—(281) 142
- M. Tuvikene: On Apodizing Diaphragms and Diaphragms Increasing Resolving Power—(284) 144
- S. Neporent and O. V. Stolbova: The Orientation Photodichroism of Viscous Solutions—(287) 146
- No. 3—March 1961**
- B. Kukanov: On the Quantum Theory of the Vavilov-Cherenkov Radiation Emitted by a Particle with a Magnetic Moment—(289) 147
- I. Agarbiceanu, L. Blaranu, V. Draganescu, N. J. Ionesco-Pallas, N. Komanichu, and V. Tatu: Determination of the Nuclear Magnetic Moment of the Hg^{199} from the Hyperfine Structure of the $\text{HgI } 5461 \text{ \AA}$ Line—(297) 151
- Draganescu: Determination of the Nuclear Magnetic Moment of Na^{23} from the Hyperfine Structure of the Absorption Lines D_1 and D_2 —(301) 152
- Kh. Propin: Calculation of the Probability of Auto-ionization in He^- and Be^+ Ions—(308) 155
- P. Dronov, A. G. Sviridov, and N. N. Sobolev: Study of the State of Krypton Behind a Shock Wave—(312) 157
- N. Bogomolov: Vibrational Spectra of Aromatic Compounds. VIII. Characteristic Vibrations of 1,2-Ortho-disubstituted Benzenes—(322) 162
- A. Kovner and B. N. Snegirev: Vibrational Spectra of Aromatic Compounds. IX. Theoretical Calculation of Intensities in the Infrared Spectra of Benzene and Certain Deuteriobenzenes—(328) 165
- Ya. Gotlib and L. V. Kudinskaya: The Theory of the Vibrational Spectra of Polymers. III. The Calculation and Interpretation of the Vibrational Spectrum of Polyethylene—(335) 168
- G. P. Stavitskaya and Ya. I. Ryskin: The Hydrogen Bond in Acid Germanates. I. The Infrared Spectrum of Strontium Dihydrogermanate—(343) 172
- A. I. Stekhanov and M. B. Eliashberg—Second Order Raman Spectra of Alkali-Halide Mixed Crystals—(348) 174
- I. M. Rozman: Excitation Energy Transfer in Rigid Solutions of Organic Substances—(354) 178
- E. G. Baronova and V. L. Levshin: Nature of Binding in the Associated Molecules of Rhodamins 3B and 6G in Aqueous Solution and the Effect of Concentration and Temperature on Migration Quenching—(362) 182
- A. A. Kaplyanskii, N. A. Moskvina, and A. K. Przhevskii: Band Splitting in the Luminescence Spectra of Anisotropic Centers in LiF and CaF_2 -Eu Crystals Subjected to Oriented Deformation—(368) 185
- L. A. Vinokurov and M. V. Fok: Determination of Electron Trap Depth in ZnS Phosphors by Flash Under the Action of Infrared Light—(374) 188
- A. F. Lubchenko: Cotton-Mouton Effect in the Region of the Impurity Absorption of Light—(379) 191
- P. G. Kard: Theory of Multilayer Asymmetric Reflectors—(384) 193
- S. L. Mandel'stam and V. V. Nedler: On the Sensitivity of Emission Spectral Analysis—(390) 196
- F. A. Korolev and Iu. K. Kvaratskheli: The Plasmatron (Plasma Jet) as a Light Source for Spectroscopy—(398) 200
- V. I. Odintsov: An Atomic Beam as Light Source for Studying Spectra of Gases—(403) 202
- I. M. Belousova and D. B. Gurevich: The Distribution of Atoms Among the Excited Levels in a Low Pressure Arc—(410) 206
- L. A. Gribov: A New Derivation of Expressions for Internal Vibrational Coordinates in Terms of Atomic Displacements in Polyatomic Molecules—(412) 208
- V. A. Kolesova: Infrared Absorption Spectra of Synthetic Aluminates of the Alkali and Alkaline-Earth Metals—(414) 209
- E. F. Gross and F. I. Kreingold: The Infrared Absorption Spectrum of Silver Oxide—(417) 211
- Ya. S. Bobovich: The Raman Spectrum of Titanite (Sphene) CaTiOSiO_4 —(418) 212
- L. N. Ovander: The Connection Between the Absorption Spectrum and the Dependence of the Raman Spectrum on the Frequency of the Incident Light—(420) 213
- Conference in East Germany on Optics and Spectroscopy at All Wavelengths—(423) 214
- A. N. Zakhar'evskii: L. Martin: Technical Optics (Translated from the English by M. V. Leikin under the Editorship of G. G. Slyusarev.)—(424) 215
- B. Sveshnikov: Sergei Ivanovich Vavilov—(426) 216
- No. 4—April 1961**
- Yu. I. Ostrovskii and N. P. Penkin: Oscillator Strengths of the Spectral Lines of Calcium—(429) 219
- A. M. Shukhtin: Interferometric Method for the Determination of the Gas Density and Electron Concentration in Plasma—(436) 222
- E. E. Nikitin: Wave Functions of Diatomic Molecules with Strong Spin-Orbit Coupling—(443) 227
- V. N. Soshnikov: Influence of the Rotational Structure of Molecular Bands on Light Absorption by Layers of Finite Thickness—(448) 229

- M. A. Kovner, Yu. S. Korostelev, and V. I. Berezin: Vibrational Spectra of Aromatic Compounds. X. Calculation and Interpretation of the Vibrational Spectra of Pyridine and the Deuteriopyridines. Nonplanar Vibrations—(457) 233
- A. S. Cherkasov and G. I. Dragneva: Influence of Solvent Viscosity on the Fluorescence Spectra of Certain Organic Compounds—(466) 238
- M. S. Brodin and S. V. Marisova: On Davydov Splitting and Polarization Ratio in the Region of the First Electronic Transition of Anthracene Crystal—(473) 242
- A. F. Lubchenko: Magnetic Rotation of the Plane of Polarization of Light in the Impurity Absorption Region—(477) 244
- I. V. Abarenkov, N. N. Kristofel' and M. I. Petrashen': Calculation of the Optical Properties of Small-Radius Electronic Centers in Ionic Crystals—(487) 250
- A. G. Cheban: On the Theory of Thermal Ionization of F⁻-Centers—(493) 253
- I. A. Parfianovich and E. I. Shuraleva: Details of the Mechanism of Phosphorescence Stimulated by Light from the F-Band Region—(500) 257
- V. L. Levshin and B. D. Ryzhikov: Dependence of Yield and Other Optical Properties of Zinc Sulfide Phosphors on the Size of Uncrushed Crystals—(505) 259
- A. I. Slutsker and V. A. Marikhin: Measurement of the Transmittance of a Light-Scattering Medium as a Method of Studying Inhomogeneities in It—(512) 263
- M. S. Kashtan and T. N. Khlopina: Increase of Precision in Isotopic Spectral Analysis—(518) 266
- Ya. D. Raikhsbaum and V. D. Malykh: On a Possible Cause of the "Carrier" Effect in Spectral Analysis—(524) 269
- A. S. Toporets: An Integrating Sphere Attachment to the SF-4 Spectrophotometer for Measurement of Diffuse Reflection and Transmission Coefficients—(528) 272
- V. A. Timofeeva: A Method of Determining Separately the Coefficients of Absorption and Scattering in Turbid Media—(533) 275
- S. I. Kubarev: On the Influence of Vibrations on the Limiting Polarization of the Luminescence of Complex Molecules—(535) 276
- A. E. Stanevich and N. G. Yaroslavskii: Absorption of Liquid Water in the Long-Wavelength Part of the Infrared Spectrum (42-2000 μ)—(538) 278
- I. F. Balashov, M. P. Vanyukov, V. R. Muratov, and E. V. Nilov: Registration of Time-Resolved Contours of Spectral Lines by Means of an Electron-Optical Converter—(540) 279
- V. A. Kizel' and V. I. Permogorov: Photoelectric Spectropolarimeter—(541) 281
- T. M. Vember and A. S. Cherkasov: Effect of p-Toluidene and Potassium Iodide on the Fluorescence and Photooxidation of 9,10-di-n-Propylantracene—(544) 282
- V. M. Zakharova and Yu. M. Kagan: Spectroscopic Determination of Ion Mobilities in Mixtures of Rare Gases—(547) 284
- V. I. Gribkov, N. D. Zhevandrov, and Sh. D. Khan-Magometova: Polarization of the Luminescence from Molecular Crystals under β -ray Excitation—(549) 285
- G. S. Gordadze: Dissociation in Sensitized Photochemical Reactions—(551) 287
- G. P. Shipulo: The Rotational Spectrum of the Cyanide Molecule—(553) 288
- L. L. Nagornaya, V. D. Bezuglyi and A. P. Grekov: A Study of the Photoluminescence and Scintillation Properties of Some 1,3,4-Oxadiazole Derivatives in Polystyrene—(555) 289
- L. Ya. Malkes, L. L. Nagornaya, and A. I. Timchenko: The Luminescence Spectra and Scintillation Properties of Para-Monohalogen Substituted Trans-Stilbene—(557) 291
- V. P. Klochkov: On the Question of the Nature of the Electronic States of Bianthrone in the Phenomena of Thermochromy and Photochromy—(559) 292
- M. P. Vanyukov, V. R. Muratov and I. A. Mukhitdinova: Time-Resolved Emission Spectra of a Spark Discharge in Nitrogen and in Air in the Wavelength Range 5000-10000 Å—(561) 294
- A. A. Mal'tsev and V. M. Tatevskii: On the Interpretation of the Infrared Spectra of the B₂O₃ and B₂S₃ Molecules—(564) 295

No. 5—May 1961

- L. M. Biberman, G. E. Norman, and K. N. Ulyanov: On the Calculation of Photoionization Absorption in Atomic Gases—(565) 297
- A. N. Zaidel' and E. P. Korennoi: Spectral Determination of the Isotopic Composition and Concentration of Lithium in Solutions—(570) 299
- K. A. Oganezov and R. R. Shvangiradze: Intensity Distribution in the Rotational Structure of Spectra of Isotopic Nitrogen Molecules and Isotopic Analysis—(577) 303
- R. R. Shvangiradze and Sh. Z. Dzhamagidze: Study of the Infrared Spectra of Isotopic Oxides of Nitrogen—(583) 306
- N. A. Borisevich and N. N. Khovratovich: Investigation of the Molecular Interactions of Phthalimides with the Aid of Their Infrared Spectra—(589) 309
- E. A. Gastilovich, D. N. Shigorin, E. P. Gracheva, I. A. Chekula, and M. F. Shostakovskii: Investigation of the Nature of Complexes of Acetylene and its Derivatives by Infrared Absorption Spectroscopy—(595) 311
- D. N. Shigorin and Yu. I. Kozlov: Study of the Free Radicals of the Triphenylmethyl Series Using Luminescence Spectra—(600) 315
- A. Ya. Khesina: Emission and Absorption Spectra of Frozen Crystalline Solutions of Certain Pyrene Derivatives—(607) 319
- A. V. Shablya and A. N. Terenin: The Phototransfer of a Proton in Acridine Derivatives at Low Temperatures as Observed in the Luminescence Spectrum—(617) 324
- A. M. Sarzhevskii: The Influence of Temperature and Viscosity on the Polarization of Fluorescence in Phthalimides—(621) 326
- V. L. Broude and M. I. Onoprienko: Absorption Spectra of Crystals of Ordinary and Deuterated Benzenes at 20°K—(634) 333
- E. G. Chernevskaya: Transmittance of Mixed CaF₂-SrF₂ and SrF₂-BaF₂ Monocrystals and the Effect of Gamma Radiation on Them—(640) 337
- V. V. Antonov-Romanovskii: Phosphor Glow Curves whose Duration of Electron Stay in Various Kinds of Traps is Comparable—(644) 339
- V. M. Belous and N. G. D'yachenko: The Effect of Infrared Light on the Luminescence of Silver Chloride—(649) 341
- S. N. Pen'kov: On the Possibility of Measuring Optical Anisotropy of Liquids in the Field of the Sound Velocity Gradient—(653) 343

- P. Kozyrev and M. A. Kropotkin: Study of Spectral Reflection Coefficients of Thermal Radiation Receiver Coatings for the Wavelength Range from 10 to 200μ —(657) 345
- P. Koslov and E. O. Fedorova: Effect of the Resolving Power of a Spectral Instrument on the Accuracy of Determining the Integral Transmission—(663) 348
- G. Kaminskii: Some Problems of the Theory of the Galvanometer When Used in Phosphorescopic Measurements—(667) 350
- N. Zaidel, G. V. Ostrovskaya, and A. A. Petrov: A Spectroscopic Method for the Determination of the Isotopic Composition of Nitrogen—(673) 353
- A. Pipinis: A Simultaneous Study of Photostimulated and Thermostimulated Luminescence and Electron Emission in Alkali Halide Phosphors—(676) 355
- A. Parfianovich and E. I. Shuraleva: The Ratio of the Optical and Thermal Light Sums in a NaCl:Ni Phosphor—(680) 358
- P. Kryzhanovskii: Reflection of Semiconducting Indium Oxide Films in the Infrared Spectral Region—(682) 359
- P. Rombakh: The Fundamental Absorption Edge of Alkaline Earth Chalcogenides—(683) 360
- F. Sheka: The Nature of the First Intrinsic Absorption Bands in Crystalline Naphthalene—(684) 360
- Memorization of S. I. Vavilov—(687) 362
- Presentation of the 1961 S. I. Vavilov Gold Medal—(691) 365
- M. Chulanovskii Honored Worker in Science and Technology of the Russian Soviet Federated Socialist Republic—(691) 365
- Conference of the Coordinating Group on the Theory of the Vibrational Spectra of Polyatomic Molecules—(692) 366
- No. 6—June 1961
- G. Veselov, I. M. Antonova, V. F. Brattsev, and I. V. Kirillova: Tables of Analytic Wave Function Parameters of Atoms and Ions—(693) 367
- G. Zhiglinskii, A. N. Zaidel', and E. A. Karklina: Study of a Direct Current Arc at Increased Pressure—(697) 368
- M. Sverdlov: On the Applicability of the Zeroth Approximation of the Generalized Valence-Optical Scheme—(702) 371
- F. Kovalev: Vibrational Spectrum and Force Field of the Trimethylchlorosilane Molecule—(707) 374
- V. Rakov: Temperature Dependence of Line Width in the Raman Spectra of Crystalline Substances—(713) 377
- N. G. Bakhshiev: Universal Molecular Interactions and Their Effect on the Position of the Electronic Spectra of Molecules in Two-Component Solutions. I. Theory (Liquid Solutions)—(717) 379
- A. F. Lubchenko: Characteristics of Light Absorption, and Luminescence in Low-Concentration Solid Binary Solutions—(727) 384
- K. N. Solov'ev: Interpretation of the Electronic Spectra of Porphyrins on the Basis of Symmetry Considerations—(737) 389
- O. P. Kharitonova: Absorption by Vapors of Organic Compounds. II. Bibenzyl and Stilbene—(745) 394
- G. P. Gurinovich, A. N. Sevchenko, and K. N. Solov'ev: Intrinsic Polarization of the Fluorescence of Porphyrins—(750) 396
- L. V. Levshin and V. K. Gorshkov: Study of the Nature of the Bonding Forces of Associated Dye Molecules in Concentrated Solutions—(759) 401
- N. A. Izmailov and E. L. Gurevich: Study of the Equilibria in Nonaqueous Solutions of Electrolytes by Means of Absorption Spectra. II. Picric Acid and Sodium Picrate in Acetic Acid, Pyridine, Acetonitrile, and Acetone—(767) 405
- L. Drozd and V. L. Levshin: The Spectral Distribution of Radiation from Nonactivated ZnS-CdS Phosphors as a Function of Temperature—(773) 408
- Errata to Vol. 10 (February issue)—(825) 411
- N. N. Grigor'ev and Yu. A. Kulyupin: The Deterioration of a Phosphor During Electroluminescence—(780) 412
- S. N. Pen'kov: A Method for Measuring Small Optical Anisotropy—(787) 416
- A. G. Zhiglinskii, A. N. Zaidel', and G. G. Kund: An Autocollimation System for Photoelectric Recording of Hyperfine Structure—(792) 418
- N. N. Vyshinskii and N. K. Rudnevskii: Vibrational Spectra of Certain Organometallic Compounds of the Group IV Elements—(797) 421
- A. I. Stekhanov, E. A. Popova, and A. A. Klochikhin: Infrared Absorption Spectra of Sodium Dihydrogen Phosphate—(799) 423
- I. S. Marshak: Repetitive Action Pulsed Light Source Based on Electric Explosion of Wires—(801) 424
- E. D. Bugrim, A. I. Lyutyi, and V. S. Rossikhin: The Occurrence of the Green MgH Bands in the Flame Spectrum—(804) 426
- A. O. Sall': Effect of Superposition of the Absorption Spectra of the Component Being Determined and an Interfering Component in Absorption Spectral Analysis—(806) 428
- S. S. Batsanov and Yu. I. Vesnin: The Refraction of Liquid HF—(808) 429
- I. N. Shklyarevskii: On the Article "The Absorption and Dispersion of Thin Gold Films" by A. N. Tekuchev—(810) 430
- Author List, Vol. X—(811) 432
- Contents List, Vol. X—434

THE M. V. LOMONOSOV PRIZE COMPETITION

(832)

The Physico-Mathematical Sciences Division of the USSR Academy of Sciences announces a competition for the M. V. Lomonosov prize, the next award of which will be made in October, 1961.

The M. V. Lomonosov prize of 2000 roubles is awarded every three years for outstanding scientific research, discovery, or invention in the field of physics. Entries for the competition may be submitted by scientific research institutes, by higher educational establishments, by design offices, by scientific and engineering societies, by active and corresponding members of the USSR Academy of Sciences and of the Academies of Sciences of the Union republics, by the scientific and engineering councils of the Ministries, Departments, and Councils of National Economy, and by Scientific Councils on the chief problems of science.

The prize is awarded for a single outstanding scientific paper, for an outstanding scientific discovery or invention, and also for a series of papers on a single theme. As a rule only an individual, personally, may compete for the prize. An exception is made for small groups of authors of a paper (or of a series of papers on a single theme, who are allowed to compete; in this case

only the senior authors are recommended for the prize.

The papers are to be submitted in three copies to the commission of experts for the award of the M. V. Lomonosov Prize at the address: Moscow, V-17, Leninskii Prospekt, 14, Division of Physico-Mathematical Sciences of the USSR Academy of Sciences, with the inscription "For the M. V. Lomonosov Prize Competition."

Organizations or individuals presenting candidates for the prize are required to submit to the Division the following documents with the inscription "For the M. V. Lomonosov Prize Competition":

1. A recommendation including the scientific nature of the paper, its significance for the development of science and the national economy, and also information on the main scientific papers, discoveries, or inventions of the author.

2. The published scientific paper (series of papers) or documents on the scientific discovery or invention, in three copies.

Papers previously awarded a prize may not be submitted.

Closing date—September 30, 1961.

ABBREVIATIONS FOR JOURNALS, PLACES, ETC. OFTEN REFERRED TO IN "OPTICS AND SPECTROSCOPY"***

- Doklady Akad. Nauk SSSR - Proceedings of the Academy of Sciences of the USSR
- Izvest. Akad. Nauk SSSR - Bulletin of the Academy of Sciences of the USSR
 Ser. Fiz. - Physical Series
 Ser. Mat. - Mathematical Series
 Otdel Khim. Nauk - Chemical Sciences Section
- Uspekhi Fiz. Nauk - Advances in Physical Sciences
- Uspekhi Khim. - Advances in Chemistry
- Zhur. Eksptl. i Teoret. Fiz. - Journal of Experimental and Theoretical Physics
- Zhur. Tekh. Fiz. - Journal of Technical Physics
- Zhur. Obshchei Khim. - Journal of General Chemistry
- Zhur. Priklad. Khim. - Journal of Applied Chemistry
- Zhur. Russ. Fiz.-Khim. Obshchestva - Journal of the Russian Physical-Chemical Society
- Zhur. Fiz. Khim. - Journal of Physical Society
- Trudy Fiz. Inst., Akad. Nauk SSSR, Fiz. Inst. im. P.N. Lebedev - Transactions of the Institute of Physics, Academy of Sciences of the USSR, named for P.N. Lebedev
- Trudy Fiz.-Tekh. Inst., Akad. Nauk Uzbek. SSR - Transactions of the Physico-Technical Institute, Academy of Sciences of the Uzbek SSR
- Trudy Inst. Krist., Akad. Nauk SSSR - Transactions of the Institute of Crystallography, Academy of Sciences of the USSR
- Trudy Inst. Nefti, Akad. Nauk SSSR - Transactions of the Petroleum Institute, Academy of Sciences of the USSR
- Trudy Gosudarst. Opt. Inst., Leningrad - Transactions of the Optical Institute in Leningrad
- Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. SSR - Transactions of the Institute of Physics and Astronomy, Academy of Sciences of the Estonian SSR
- Trudy Inst. Fiz., Akad. Nauk Ukr. SSR - Transactions of the Institute of Physics, Academy of Sciences of the Ukrainian SSR
- Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Metrol. - Transactions of the All-Union Scientific Research Institute of Meteorology
- Vestnik Leningrad. Univ. - Bulletin of the Leningrad University
 Ser. Fiz. i Khim. - Series on Physics and Chemistry
- Gosudarst. Opt. Inst. - State Optical Institute
- Moskov. Fiz.-Tekh. Inst. - Moscow Physico-Technical Institute
- Izd. Inostrannoi Lit. - Publishers of Foreign Literature
- Izd. Akad. Nauk SSSR - Academy of Sciences Press
- Vestnik Moskov. Univ. - Bulletin of Moscow University
 Ser. Fiz.-Mat. i Estestven. Nauk - Series of Physical-Mathematical and Natural Sciences
- Uchenye Zapiski Leningrad. Gosudarst. Univ. im. A. A. Zhdanov - Scientific Reports of the Leningrad State University named for A. A. Zhdanov
 Ser. Fiz. Nauk - Series on the Physical Sciences
 Ser. Khim. Nauk - Series on the Chemical Sciences
- Uchenye Zapiski, Moskov. Gosudarst. Univ. im. M. V. Lomonosova - Scientific Reports, M.V. Lomonosov Moscow State University
- Uchenye Zapiski Tomsk. Gosudarst. Univ. in. V. V. Kuibysheva - Scientific Reports of the Tomsk State University named for V. V. Kuibyshev
- Opt. i Spekt. - Optics and Spectroscopy
- Pribory i Tekh. Ekspt. - Instruments and Technique of Experiment
- Astron. Zhur. - Astronomical Journal
- Fiz. Metal. i Metalloved., Akad. Nauk SSSR, Ural. Filial - Physics of Metal and Metallography, Academy of Sciences of the USSR, Ural Branch
- PriBOROSTROENIE - Instrument Manufacturing
- Zavodskaya Lab. - Factory Laboratory
- Radiotekhnika - Radio Engineering
- Radiotekh. i Elektron. - Radio Engineering and Electronics
- Inzhener.-Fiz. Zhur., Akad. Nauk Belorus. SSR - Engineering-Physics Journal, Academy of Sciences of White Russian SSR
- Ukrain. Fiz. Zhur. - Ukrainian Physics Journal
- Automat. i Telemekh. - Automatics and Telemechanics
- Nauch.-Issledovatel. Fiz.-Tekh. Inst., Leningrad. Univ. - Scientific Research Institute of Physics and Technology, Leningrad University
- Nauch.-Issledovatel. Radio-fiz. Inst., Gor'kii Univ. - Scientific Research Institute of Radiophysics, Gorki University
- Gorkov. Issledovatel. Fiz. Tekh. Inst. - Gorki Research Institute of Physics and Technology
- Gosudarst. Izd. Tekh.-Teoret. Lit. - State Publishers of Technical-Theoretical Literature
- Gosudarst. Izd. Fiz.-Mat. Lit. - State Publishers of Physical-Mathematical Literature
- Inst. Fiz., Akad. Nauk Ukr. SSR, Kiev - Institute of Physics, Academy of Sciences of the Ukrainian SSR, Kiev
- Inst. Fiz. i Astron., Akad. Nauk Eston. SSR, Tartu - Institute of Physics and Astronomy, Academy of Sciences of the Estonian SSR, Tartu

***These abbreviations must be used by Ois translators in their translations. This list will be added to from time to time.

APPLIED OPTICS

to be published by The Optical Society of America

Editor: JOHN N. HOWARD, *Geophysics Research Directorate, Bedford, Mass.*

APPLIED OPTICS will publish in the areas of applied optics and closely related scientific and technical fields, e.g. physical, electron, ion, ultraviolet and space optics, lens design and optical formulas, plasma, solid state and crystal optics. **APPLIED OPTICS** will be issued bimonthly from January 1962 and will feature

..... A leader review paper on one of the major aspects of optics or its applications, e.g., new infrared detectors, new optical materials, applications of physical optics in manufacturing process control. This review will be about 10,000 words long and will set the **feature** subject of each issue.

..... Contributed technical papers—3000/5000 words each—about ten per issue—in **any area** of applied optics.

Shop and technical notes
Reports of Meetings

Book reviews
Personalia
Optical Activities in
The Universities

Letters to the Editor
Meetings Calendar
Industry

** Each issue will feature one area of applied optics, which feature will be the responsibility of a Subject Editor.

1962	JANUARY	— OPTICAL PUMPING AND MASERS	BRUCE H. BILLINGS
	MARCH	— SPACE OPTICS	LLOYD G. MUNDIE
	MAY	— FOREIGN OPTICS	DAVID Z. ROBINSON
	JULY	— OPTICAL ENGINEERING	RODERIC M. SCOTT
	SEPTEMBER	— INFRARED	JOHN N. HOWARD
	NOVEMBER	— INFORMATION THEORY	F. DOW SMITH
1963	JANUARY	— ASTRONOMY	JAMES G. BAKER
	MARCH	— INSTRUMENTATION	W. L. HYDE
	MAY	— INTERFEROMETRY	R. A. WOODSON

APPLIED OPTICS will be the one publication devoted solely to applied optics in its broadest sense and designed to meet the interests of scientists, engineers, technologists, technicians—in a word, opticians—working in optics or its applications, in fields borderline to optics and employing optical techniques.

Special prepublication rates for founder subscribers

All orders for a three year period, placed prior to publication, will be entered at the following special rate:

O.S.A. members—3 yr. sub. \$15.00

Non-members—3 yr. sub. \$25.00

Yearly subscription rates will be

O.S.A. members—\$6.00

Other AIP Societies members—\$8.00

Non-members—\$10.00

Subscriptions and inquiries should be sent to

Optical Society of America

1155 Sixteenth Street, N.W., Washington 6, D.C.

IMPORTANT NOTICE TO ALL READERS OF OPTICS AND SPECTROSCOPY

OIS CLUB SCHEME

The Optical Society of America has been translating Optika i Spektroskopiya and distributing this monthly journal free - thanks to an NSF grant - to all OSA members and subscribers to the Journal of the Optical Society of America. This free distribution was an experiment for three years, so that the individual reader might become accustomed to reading a translation journal not as an oddity but as a publication that is looked for each month in the same manner as is J. Chem. Phys., J. Am. Chem. Soc., etc. In December of this year the NSF grant ends, but the interest in Optics and Spectroscopy is now too lively for OSA to discontinue the translation, so they have evolved the OIS CLUB SCHEME.

Put simply, this is a special subscription rate for members of those societies who wish to take part in the OIS CLUB SCHEME, viz:

To OSA members -----	\$ 7.50
To members of the Ois Club -----	\$11.00
To non-members -----	\$15.00

OSA is emphatic that if a translation journal is to be of real use (as is the case with any scientific journal) it should be read widely by all the people working in the field, and that these research results should be made available in the shortest possible time. OPTICS AND SPECTROSCOPY is published in English translation within three months of the Russian edition coming out e.g. the March 1961 issue will be published in English on June 10th. OSA is making this special offer to members of some sixty scientific societies across the English speaking world, and it asks the members of those Societies to write to their Society or directly to the Assistant Secretary, OSA, 1155 16th St., N.W., Washington 6, D.C. for further details or to send in their order. (see below)

ALL SUBSCRIBERS PLEASE NOTE that your subscriptions will start with the January 1962 issue which is published in English in March/April 1962 -- so don't start worrying when the January 1962 issue does not appear in that month!

ORDER FORM

To: OPTICS AND SPECTROSCOPY
Optical Society of America
1155 Sixteenth St., N.W.
Washington 6, D.C.

Please enter my/our subscription to OPTICS AND SPECTROSCOPY for one year commencing with the January 1962 issue (which will be published in April), at:

☐ <u>Special OSA member rate</u>	\$ 7.50
☐ <u>Special rate to members of Societies cooperating in Ois Club Scheme</u>	\$11.00

Name of your Society _____

☐ Non-members	\$15.00
☐ Please send OSA membership information	

Membership no. _____

Name _____

Address _____

FILLER MATERIAL - NOT

IN RUSSIAN ORIGINAL

OPTICAL SOCIETY *of* AMERICA

OSA CHARTER FLIGHT TO EUROPE, AUGUST 1962

OSA hopes to arrange a charter flight to Europe for the month of August, 1962, for members attending the Munich ICO Meeting August 20 - 25.

We contemplate a flight leaving New York (Idlewild) on Monday, 30th July for Paris, and returning from Munich Airport on Monday, 27th August to New York. Members would make their own way between Paris and Munich. It is necessary to make arrangements for such flight within the next month or two, so we need now an expression of interest (without commitment, of course) from members. Members who are interested in principle should return the bottom half of this page to the Executive Office as soon as possible, or hand it in at the Registration Desk during the course of the Los Angeles Fall Meeting. The round trip fare - New York - Paris - Munich - New York - would be about \$275.00.

REPLY

Assistant Secretary,
OPTICAL SOCIETY OF AMERICA
1155 Sixteenth Street, N.W.
Washington 6, D. C.

CHARTER FLIGHT AUGUST, 1962

I am interested in principle in a charter flight N. Y. - Paris - Munich - N. Y. August, 1962.

Name _____ Membership No. _____

Address _____

(FILLER MATERIAL - NOT IN RUSSIAN ORIGINAL)

TRANSLITERATION OF CYRILLIC CHARACTERS

used by the Optical Society of America

А	а	a	Р	р	r
Б	б	b	С	с	s
В	в	v	Т	т	t
Г	г	g	У	у	u
Д	д	d	Ф	ф	f
Е	е	e	Х	х	kh
Ж	ж	zh	Ц	ц	ts
З	з	z	Ч	ч	ch
И	и	i	Ш	ш	sh
Й	й	i	Щ	щ	shch
К	к	k	Ъ	ъ	"
Л	л	l	Ы	ы	y
М	м	m	Ь	ь	'
Н	н	n	Э	э	e
О	о	o	Ю	ю	yu
П	п	p	Я	я	ya

(FILLER MATERIAL - NOT IN RUSSIAN ORIGINAL)

EDITOR'S NOTE

Comments on the scientific content of the translated Russian articles published in OPTICS AND SPECTROSCOPY are invited. They should be addressed as a Letter to the Editor of the Journal of the Optical Society of America and forwarded to the Editor of that journal, Dr. D. B. Judd, National Bureau of Standards, Washington 25, D. C.

CONTENTS

(Numbers in parentheses are original Russian page numbers.
These Russian page numbers are also quoted at the head of each paper.)

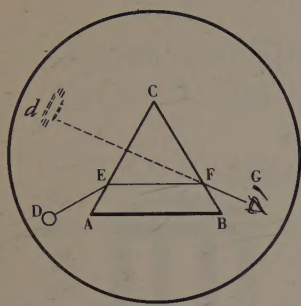
Tables of Analytic Wave Function Parameters of Atoms and Ions	367	(693)
Study of a Direct Current Arc at Increased Pressure	368	(697)
On the Applicability of the Zeroth Approximation of the Generalized Valence-Optical Scheme	371	(702)
Vibrational Spectrum and Force Field of the Trimethylchlorosilane Molecule	374	(707)
Temperature Dependence of Line Width in the Raman Spectra of Crystalline Substances	377	(713)
Universal Molecular Interactions and Their Effect on the Position of the Electronic Spectra of Molecules in Two-Component Solutions. I. Theory (Liquid Solutions).	379	(717)
Characteristics of Light Absorption and Luminescence in Low-Concentration Solid Binary Solutions	384	(727)
Interpretation of the Electronic Spectra of Porphyrins on the Basis of Symmetry Considerations	389	(737)
Absorption by Vapors of Organic Compounds. II. Bibenzyl and Stilbene	394	(745)
Intrinsic Polarization of the Fluorescence of Porphyrins	396	(750)
Study of the Nature of the Bonding Forces of Associated Dye Molecules in Concentrated Solutions	401	(759)
Study of the Equilibria in Nonaqueous Solutions of Electrolytes by Means of Absorption Spectra. II. Picric Acid and Sodium Picrate in Acetic Acid, Pyridine, Acetonitrile, and Acetone	405	(767)
The Spectral Distribution of Radiation from Nonactivated ZnS-CdS Phosphors as a Function of Temperature	408	(773)
Errata to Vol. 10 (February issue).	411	(811)
The Deterioration of a Phosphor During Electroluminescence	412	(780)
A Method for Measuring Small Optical Anisotropy	416	(787)
An Autocollimation System for Photoelectric Recording of Hyperfine Structure	418	(792)

SHORT COMMUNICATIONS

Vibrational Spectra of Certain Organometallic Compounds of the Group IV Elements	421	(797)
Infrared Absorption Spectra of Sodium Dihydrogen Phosphate	423	(799)
Repetitive Action Pulsed Light Source Based on Electric Explosion of Wires	424	(801)
The Occurrence of the Green MgH Bands in the Flame Spectrum	426	(804)
Effect of Superposition of the Absorption Spectra of the Component Being Determined and an Interfering Component in Absorption Spectral Analysis	428	(806)
The Refraction of Liquid HF	429	(808)

LETTERS TO THE EDITOR

On the Article "The Absorption and Dispersion of Thin Gold Films" by A. N. Tekuchev	430	(810)
Author List, Vol. X	432	(811)
Contents List, Vol. X	434	



optics and spectroscopy

volume xi

OPTICAL SOCIETY OF AMERICA

USSR ACADEMY OF SCIENCES

RUSSIAN EDITORIAL STAFF FOR
OPTIKA I SPEKTROSKOPIYA sponsored by
USSR ACADEMY OF SCIENCES

Editor: S. E. FRISH

Assistant Editor: P. P. FEOFILOV

Corresponding Secretary: L. S. SAZONOV

Associate Editors:

M. V. VOLKENSTEIN	V. P. LINNIK	N. N. SOBOLEV
M. M. GUREVICH	S. L. MANDEL'SHTAM	A. N. TERENIN
M. A. EL'IASHEVICH	I. V. OBREIMOV	A. I. TUDOROVSKII
A. A. LEBEDEV	V. K. PROKOF'EV	V. M. CHULANOVSKII

Translated from *OPTIKA I SPEKTROSKOPIYA* on the initiative of THE OPTICAL SOCIETY OF AMERICA, INC. with a grant-in-aid from THE NATIONAL SCIENCE FOUNDATION. *Optics and Spectroscopy* is a cover-to-cover translation of *Optika i Spektroskopiya* and no attempt is made to edit the material other than to correct obvious misprints. The views are those of the original authors and do not represent the Optical Society of America.

TRANSLATION EDITORIAL STAFF

Scientific Editors

CYRUS FELDMAN, *Oak Ridge National Laboratory*

CARL W. GARLAND, *Massachusetts Institute of Technology*

MATHEW G. GIBBONS, *Oakland, California*

Administrative Editor:

PATRICIA R. WAKELING, *OSA*

Published monthly by the Optical Society of America, Inc. Executive office: 1155 Sixteenth Street, N.W., Washington, D.C. Subscriptions for one year to members of the Society: Associates \$13.00; Regular members and Fellows \$17.00. Subscriptions for non-members of the Society: One year U. S. and Possessions, \$25.00; Foreign \$28.00. Back numbers: \$3.00 per copy. Subscriptions, changes of address and undeliverable copies should be referred to the Executive offices in Washington, D.C. The office of publication is 2500 South State Street, Ann Arbor, Michigan. Second class postage paid at Ann Arbor, Michigan.